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ADVANCED WASTE TREATMENT RESEARCH PROGRAM, JULY 1964-JULY 1967

Federal Water Pollution Control Administration
Cincinnati, Ohio

1968

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WATER POLLUTION CONTROL RESEARCH SERIES
Advanced Waste Treatment Research

SUMMARY REPORT
Advanced Waste Treatment

JULY, 1964 – JULY, 1967

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U.S. DEPARTMENT OF THE INTERIOR
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AWTR–Waste-Treatment Processes

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Water Pollution Control Research Series Publication No. WP-20-AWTR-19

WPCR SUB-SERIES

Waste-Treatment Processes (AWTR). A variety of methods have been used to remove part of the pollutants from wastewater before it is discharged. In many situations, existing methods are not adequate to provide the degree of treatment required to control pollution effectively. Research in waste treatment is being directed at developing methods ranging from lower-cost or higher-efficiency versions of conventional treatment technology to total wastewater purification systems capable of removing virtually all pollutants and even of producing reusable effluents. The Federal Water Pollution Control Administration's research in this area covers the entire field of waste treatment including treatment of industrial wastes, with special emphasis given to waste-treatment methods capable of total pollution control and purification of wastewater for deliberate reuse. This subseries, Waste-Treatment Processes, contains reports on results of this research by the Administration.

ADVANCED WASTE TREATMENT RESEARCH PUBLICATIONS

		Report Number
AWTR-1	Summary Report, June 1960 - December 1961	W62-9
AWTR-2	Preliminary Appraisal of Advanced Waste Treatment Processes	W62-24
AWTR-3	Ultimate Disposal of Advanced-Treatment Waste	999-WP-3
	Part 1. Wet Oxidation Part 2. Incineration	
AWTR-4	Waste-Water Renovation	999-WP-4
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AWTR-8	Ultimate Disposal of Advanced-Treatment Waste Part 1. Injection Part 2. Placement in Underground Cavities Part 3. Spreading	999-WP-10
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AWTR-12	Evaluation of Various Adsorbents and Coagulants for Waste-Water Renovation	999-WP-14
AWTR-13	Electrochemical Treatment of Municipal Waste Water	999-WP-19
AWTR-14	Summary Report: The Advanced Waste Treatment Research Program. January 1962 through June 1964	999-WP-24
AWTR-15	Feasibility of Granular, Activated Carbon Adsorption for Waste-Water Renovation. 2.	999-WP-28
AWTR-16	Adsorption of Biochemically Resistant Materials from Solution. 2.	999-WP-33
AWTR-17	Studies Relating to Market Projections for Advanced Waste Treatment	WP-20-AWTR-17
AWTR-18	Electrodialysis in Advanced Waste Treatment	WP-20-AWTR-18
AWTR-19	Summary Report: Advanced Waste Treatment Research Program July 1964 - July 1967	WP-20-AWTR-19

FOREWORD

There are two ultimate objectives to advanced waste-treatment. One is to help alleviate the Nation's increasing water pollution problem, and the other is to renovate wastewater for deliberate reuse.

A program to study advanced waste-treatment methods was instituted by the U.S. Public Health Service at the Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio in July 1960, and received specific authorization in July 1961, with passage of the amendments to the Federal Water Pollution Control Act (Public Law 87-88). On December 31, 1965, Congress created the Federal Water Pollution Control Administration (FWPCA) within the Department of Health, Education, and Welfare. At that time, the Advanced Waste Treatment Research Program was transferred from the Public Health Service to the new Administration. In May 1966, the FWPCA was transferred to the Department of the Interior. An Advanced Waste Treatment Branch was formed in the Division of Research, Office of Research and Development where studies are continuing.

Results of advanced waste-treatment studies through June 1964 have been summarized in two publications, AWTR-1 and AWTR-14. Detailed project reports (see pp. iii and iv for listing) have also been issued. This report summarizes results of studies carried out from July 1964 to July 1967 .

* * * * *

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ABSTRACT

This report summarizes results of advanced waste-treatment studies from July 1964 to July 1967. Under a combined program of contract and intramural research, a wide range of wastewater-treatment processes have been evaluated for technical and economic feasibility at stages of development from laboratory-scale through pilot-scale. These treatment methods include processes for suspended solids removal, organic removal, inorganic removal, nutrient removal, and ultimate disposal of concentrated end products. Since it is obvious that the efficiency of the conventional biological processes greatly affects some of the advanced processes, studies of certain aspects of the biological processes have become a part of advanced waste-treatment research.

A number of processes have been studied extensively enough to assess their feasibility with a fair degree of accuracy. For wastewaters, with appropriate contaminant composition, lime clarification will effectively remove suspended solids and the nutrient phosphate. Since this method of treatment is widely used on potable water supplies, the economics are expected to be favorable. Alum clarification is expected to be a successful method of treatment in other locations at a cost of 8 cents/1,000 gal. or less for a 10-mgd plant. For organic removal, activated-carbon treatment is very promising. Granular-carbon treatment without clarification of the feed can be carried out for about 8 cents/1,000 gal. at the 10-mgd level. There will be some turbidity in the product water. Powdered-carbon treatment has been estimated to cost about 12 cents/1,000 gal. for the same capacity plant, provided the carbon can be reactivated. Process improvements, however, should reduce the cost. The powdered-carbon treatment gives a highly clarified water. The problem of reactivating powdered carbon will be intensively studied. For removal of gross inorganic content, electrodialysis treatment should be possible for about 16 cents/1,000 gal. in a 10-mgd plant. Fouling of electrodialysis membranes presents some problems. Pre-treatment of the feed by clarification and carbon treatment appears to be a necessity. Other inorganic removal processes such as ion exchange and reverse osmosis may be competitive with electrodialysis, but they have not been as extensively studied. Removal of nitrogen, either as ammonia or nitrate, is a difficult problem. An air-stripping process for ammonia appears technically feasible and should not cost over 2 cents/1,000 gal. for a 10-mgd plant, excluding the cost of adjustment of pH to 10 or above. Initial study of denitrification of a highly nitrified effluent or granular activated carbon shows promise for nitrate removal.

Study of a number of processes given preliminary evaluation has been halted, at least for the present. Electrochemical treatment appears to be economically unfavorable. The foaming process, although technically feasible for removal of certain soluble and suspended organic materials, and while economically promising, has not been generally necessary since the introduction of biodegradable anionic detergents in 1965. Solvent extraction, distillation, and freezing also have encountered a number of problems that limit their usefulness.

INTRODUCTION

Advanced waste-treatment refers to methods and processes that will remove more contaminants from wastewater than are usually removed in present day conventional treatment plants. The processes may be physical-chemical, or biological. Certain of these are routinely used in technologies other than the water field.

There are two important reasons for studying advanced waste-treating methods. First is the pressing need for developing means to provide better water pollution control than is now possible. The effluent streams discharged from the most effectively run conventional treatment plants contain soluble and suspended organic compounds that exert an oxygen demand on the receiving streams. Some of the organics can also be toxic to fish and other forms of biological life in the stream. Treated effluents contain nutrients that promote excessive growth of algae in streams and lakes. In some cases the conventionally treated effluents contains undesirable amounts of minerals. Advanced treatment processes suitable for removing all types of contaminants and for disposal of the concentrated waste materials produced by such processes are being extensively researched. The second reason for studying advanced treatment techniques is to develop methods for renovating wastewaters by improving the quality of the water to such an extent that it may be directly reused. It is now generally recognized that the relatively fixed natural water supply in the United States will be inadequate to supply the water needs of a growing population and expanding industry. Renovation and reuse of the wastewater thus becomes an increasing necessity. Envisioned uses range from agricultural and industrial process water to potable water, with the degree of purification required varying according to the specific use.

Although the term "tertiary" is often used as a synonym for advanced treatment methods, the two are not precisely the same. Tertiary suggests a single treatment to be applied only after conventional primary and secondary treatment. "Advanced treatment" actually means any process, technique, or system not now in common use. The advanced treatment techniques may be used after conventional treatment, or they may modify or replace one or more steps comprising present conventional treatment. For example, if chemicals are added in the conventional activated sludge biological process to precipitate phosphorus, this is advanced treatment. Because economic considerations will largely determine the type of treatment applied to a given case, it is unlikely within the foreseeable future that advanced methods will be extensively used in place of conventional primary and secondary treatment. Municipalities should not be reluctant to construct conventional treatment plants on the assumption that they may soon become obsolete. The number of treatment techniques or processes that may be added after secondary treatment depends upon the quality requirements for the product water. A single additional process may be all that is necessary. Most advanced processes can be installed later as pollutant removal requirements become more stringent. With the concept of water reuse, improved treatment need not be looked upon as a heavy financial burden. As the quality of the treated water is improved, the value of that water is increased to compensate for the additional treatment cost.

To carry out the program of advanced waste-treatment studies, an approach involving both extramural and intramural work has been adopted. Extramural work is conducted through negotiated contracts with universities, private research institutes, and industrial organizations. The contracting mechanism has the invaluable advantage of providing in a minimum of time the services of experienced personnel who are highly specialized in many fields. Without the use of contracts the rapid screening of a large number of processes would not have been possible.

Although contract work has been, and continues to be, a useful method for carrying out advanced waste-treatment studies, intramural investigations are also essential. Most of the intramural research has been carried out at the Robert A. Taft Sanitary Engineering Center, or at pilot installations which are partially or fully administered by personnel from that laboratory. Presently, there are three advanced waste-treatment research pilot facilities. The first of these is the Pomona, California Research Facility operated jointly by FWPCA and the Los Angeles County Sanitation Districts. The facility is located on the site of the Pomona Water Renovation Plant. In addition to land and personnel, the Los Angeles County Sanitation Districts contribute significant funds for the work being carried out. A pilot-scale activated-carbon adsorption study has been in operation for over two years. This and other investigations have yielded useful data for scale-up of carbon adsorption equipment. Other processes including reverse osmosis, ion exchange, clarification, and biological denitrification are also being actively studied. The second pilot facility was constructed at Lebanon, Ohio on the grounds of the Lebanon Sewage Treatment Plant. Under a cooperative agreement, the City of Lebanon has allowed the use of their land for this installation. The original purpose of this facility was to study the electrodialysis process. From the inception, however, it was obvious that other processes also could be studied conveniently at this same site. The facility was made sufficiently large, therefore, to accommodate other pilot equipment. Studies on electrodialysis, powdered activated carbon, and suspended solids removal have been underway for over two years. The third pilot installation, the Joint FWPCA-D.C. Advanced Waste-Treatment Research Pilot Plant, is located at the District of Columbia Water Pollution Control Plant. The District of Columbia Department of Sanitary Engineering is cooperating in this work to the extent of supplying a site for the facility, all necessary utilities, and some of the labor, especially maintenance. Although operation of equipment has not begun, it is intended that a train of processes including biological treatment, chemical clarification, carbon treatment, and, possibly, demineralization will be investigated.

The Robert A. Taft Sanitary Engineering Center has a long history of research in the field of water pollution. Combinations of several disciplines have been instrumental in the development and use of many of the tools in the water pollution and measurement field. The availability of an intramural staff to review contract work and to supplement it with additional data allows accurate evaluation to be made of the feasibility of the various processes. Thus, strong intramural research and contracting make possible more rapid progress than might otherwise be obtained.

During the period covered by this report, considerable progress has been made in the development of the more promising treatment methods. A number of these have reached the stage of pilot investigation. Enough information is becoming available to attempt optimization of the processes. Some treatment methods were found infeasible and will not be studied further. New processes have been proposed, especially in regard to nutrient removal. Generally, the chance of success of newly proposed methods cannot be expected to be as high as for methods studied in the past that had often been developed, to varying degrees, for other uses. Some of the new processes appear sufficiently interesting, however, that investigation is considered necessary. This broad attack on better treatment methodology will certainly result in a much-needed improvement of our ability to control water pollution and produce reusable water.

CONVENTIONAL SEWAGE TREATMENT

At present, municipal wastewater is usually given varying degrees of treatment before being discharged into a receiving stream. The primary object of the treatment has been to reduce the amount of oxygen-demanding materials in the water along with reduction of suspended solids and bacteria. There is no doubt that the conventional processes can be made to perform better. The investigation of ways that will improve treatment by conventional methods cannot logically be separated from studies of new processes that may be added after or combined with the conventional processes. It should also be pointed out that processes added after conventional treatment may, for optimal results, require better conventional treatment than is usually available today. All treatment stages must be integrated in such a way as to give the desired quality water as economically as possible.

More and more frequently, the question arises of whether conventional treatment methods will soon be obsolete. There are inherent disadvantages to parts of a conventional system for which dependable and economical substitutes would be welcomed. Some possible substitute processes are being studied. None of these have reached the stage of development, however, where use on a plant scale can be expected in the near future. It is safe to assume that the conventional processes will have widespread application for many years. Designers, however, should take into account the future need for chemical additions at various points within plants and the present availability of processes that can be added after conventional treatment.

Principle of Operation

Conventional treatments are classed as primary and secondary. Primary treatment usually consists of coarse screening or grinding, grit removal by settling, and suspended organic removal by further settling. Removal of pollutants as measured by the 5-day biochemical oxygen demand (BOD_5) is about 35 percent.

Conventional secondary treatment consists of some form of biological oxidation. In the trickling filter process, settled effluent is sprayed over a bed of rocks or other media that accumulates microorganisms on its surface. The mixed biological life utilizes the organic materials in the wastewater for food and thus purifies the water. There is a slow sloughing-off of the organisms into the product water. These solids are removed in a final settler. Some of the product water may be recycled back through the biological bed to increase contact time.

Another common secondary treatment method is the activated sludge process. After primary settling air is bubbled through the wastewater for up to six hours. This causes growth of aerobic bacteria and other organisms which use organics in the wastewater for food. A final settler is used for removal of the organisms. A large part of the biological sludge is returned to the aeration chamber. BOD removal, including the removal by primary treatment, can reach 95 percent. This is slightly better treatment than is possible in a trickling filter.

The biological sludges that result from the oxidation processes and the sludge settled in the primary settler are wastes that must be further treated. A common treatment method is anaerobic biological digestion, followed by drying of the residue. This is then used for land fill or as a soil conditioner or, in some cases, it is burned.

Another secondary treatment method, less effective than the others, is the use of stabilization ponds. There is considerable variation in design and operation of these ponds, but in all designs the water is given a long enough residence time in shallow lakes for oxidation of organic matter to take place. Growths of algae occur in most cases. The algae are a good source of oxygen due to photosynthesis, but they contribute secondary pollution. Their removal, which is difficult, would lower the product-water BOD_5. This removal is, in fact, a subject for advanced waste-treatment study. Stabilization pond treatment is a good example of a method that may be improved by proper combination of a conventional oxidation stage with a new process to give an advanced treatment system.

System Optimization and Process Control

The designing of waste treatment plants has not been carried out in the past in such a way that a given quality water would necessarily be produced at the lowest possible cost. True optimization of plants has not been possible because of a lack of adequate mathematical descriptions for the performance of component parts. Similarly, automatic adjustment of controllable variables in response to changes in flow rate and contaminant concentration was not possible because of lack of mathematical models and measurement techniques for the various parts of the treatment system. Whether optimization and automatic control will have a significant effect on treatment cost or treatment efficiency remains to be seen. They are important enough, however, to warrant exploration, and studies are underway at Cincinnati in this area of work.

As the first step in the study of optimization and control, two principal types of mathematical models are being developed for each wastewater treatment process. Initially, primary and secondary treatment are being studied, but work will be extended to other processes later. The first mathematical model is the pseudo-steady-state model which relates the effluent stream vectors from a process to the influent stream vectors and the decision vector which specifies how the process is to be operated. Stream vectors are a list of parameters which completely characterize the stream, such as volume flow, temperature, and the concentration of up to twenty species of contaminants. The principal classification of contaminants is chemical, that is, carbon, nitrogen, phosphorus, and fixed inorganic matter. The carbon is sub-divided into biodegradable carbon and non-biodegradable carbon. Each class is further sub-divided into settleable and dissolved fractions. For processes which remove dissolved salts, the stream vector also contains the concentration of each ionic specie.

The psiudo-steady-state model is based on 24-hour composite values and is expressed in terms of material balances around control volumes. Stoichiometry, pseudo-rate constants, mixing assumptions, and assumptions about separation of phases such as occurs in settlers or filters are included in the model. Each computed effluent stream vector must be suitable for use as an influent stream vector to any other downstream process.

Models have been developed for the conventional system which included preliminary treatment, primary settling, activated sludge, sludge thickening, digestion, elutriation of sludge, vacuum filtration with addition of chemicals, and sludge incineration. A digital computer program has been developed which contains pseudo-steady-state models for these processes arranged in the most commonly used configuration. Many assumptions not fully justified by engineering investigation were made. Thus, development of the models has drawn attention to the need for additional measurements of process performance and has helped to show what additional data are needed.

A serious limitation of the existing computer program is the assumed arrangement of the processes within the system. An executive digital computer routine is being developed which will allow the performance of any set of processes arranged in any configuration to be computed without rewriting the system computer program.

The ultimate goal of the pseudo-steady-state modeling effort is to find mathematical relationships for the performance and cost of all practical wastewater renovation processes. These relationships must have sufficient validity that they can be used with confidence by plant designers and system analysts to make decisions concerning the best way to construct a system to produce water of any specified quality from any wastewater stream for which the stream vector is known.

The second principal kind of mathematical model is the time-dependent model which computes the process performance as a function of time when the influent stream or the operating decisions, or both, vary with time. One digital computer program has been completed which simulates the time-dependent behavior of the activated sludge process. This computation, which is a numerical integration utilizing the Runge-Kutta fourth-order method, integrates the Monod differential equations which express the growth of three classes of bacteria:

heterotrophic carbon users, *Nitrosomonas* which converts ammonia to nitrite, and *Nitrobacter* which converts nitrite to nitrate.

The aerator is sub-divided into ten sub-volumes, any number of which can be used to simulate mixing, and a sludge storage tank is provided in the sludge return line. A surge tank, in which no biological activity is assumed, is also provided upstream from the aerator. Sinusoidally varying flow and BOD concentration will be applied to this system, and the concentration of three classes of microorganisms and three substrates, as well as flow, will be computed as a function of time at each of seventeen stations. Various control schemes will be studied including pumping of sludge from the sludge storage tank to minimize the effect of the varying load on the plant, or the use of the surge tank to smooth out the flow. The biological growth equations were taken from the British literature and a need exists to compare the computed results with the performance of a full-size plant under a load varying with time.

The ultimate goal of the time-dependent model is to study methods for control of the activated sludge process to give optimum performance when the flow and BOD concentration entering the plant vary throughout the day.

Experimental Investigations

Two investigations involving conventional treatment have been undertaken. A third study involving removal of algae from stabilization pond effluent is discussed on page 71. One of the investigations, involving the contact stabilization method of treatment, was tested on a municipal waste with a large fraction of industrial waste. Contact stabilization is a modification of the activated sludge process that has a very short aeration time for the wastewater. The sludge that is to be returned to the aerator is, however, reaerated first in a separate tank. Using a 250-ml/min pilot system, the process was found to give up to 79 percent BOD removal with an aeration time of 25 min and a sludge reaeration time of 115 min. High product quality was not a primary aim of this work. One of the functions of the system was to supply secondary effluent for other studies.

An investigation carried out under a contract to Infilco, was undertaken to learn whether there could be a substantial saving in treatment cost if an activated sludge process with very short aeration time were combined with chemical treatment for improved removal of biological floc. Phosphorus would also be removed by the process. (Chemical treatment is described in more detail on page 15.) Short aeration under the conditions proposed produces a poorly settling sludge. A final chemical clarification would be necessary to bring the effluent BOD into the range obtained by conventional operation. From experimental results, it was concluded that aeration could be reduced to 1 hour compared to a standard of 6 hours. A lime dose of 200 mg/1 as $Ca(OH)_2$ and an alum dose of

20 mg/l were shown to be required for proper settling. Although the capital cost of the combined system was slightly less than for the standard activated sludge process, the operating cost, including amortization of equipment, was slightly higher. There does not appear to be a clear-cut advantage to the combined system except for improved phosphate removal that results from chemical addition.

Future Work

Several large-scale experimental studies are planned. Modifications of processes will be tested for the verification of the mathematical models being developed for the conventional processes. At the Washington, D.C. Pilot Plant, a very versatile system with a maximum capacity of 300 gpm is planned. Both primary and secondary treatment will be included. A flotation unit as well as a settler will be tested for removal of floc after aeration. A wide range of operating conditions will be investigated. Other operating plants will be studied.

Both mathematical development and experimental work will be included in a study that will be carried out by General American Transportation Corporation. This work will deal with the mathematical models for the treatment processes.

To optimize the design for a plant requires cost data on equipment. These data are not readily available in the literature. Contract work is planned, therefore, to obtain cost-capacity correlations for the components of a treatment plant.

SUSPENDED SOLIDS REMOVAL

Secondary effluent contains materials ranging in particle size from easily-visible, insoluble solids down through colloids to definitely soluble molecules and ions. It is impossible to precisely classify all these materials as either insoluble or soluble. There is, however, a significant amount, often 10 to 20 mg/l, of the organic material and some of the inorganic material in secondary effluent that can be removed by the various processes used to carry out clarification. These materials are usually called suspended solids. The smallest particle to be removed varies with the process. A simple straining of the water might only remove particles greater than 10 microns. The combination of flocculation, sedimentation, and filtration removes most particles down through the colloidal range and even removes some soluble materials by adsorption on the floc.

The suspended solids are detrimental for a number of reasons. They are a major source of the remaining organic pollution in secondary effluent, that is, they constitute a major part of the BOD in the water. Their removal would, therefore, significantly reduce the pollutional load on a receiving stream. The suspended solids interfere with or prevent the operation of a number of other advanced waste-treatment processes. These materials also are undesirable or prohibitive in most envisioned direct reuses of the water.

Comparatively little work was done on removal of suspended solids from secondary effluent before 1965. Within the last two years, however, several investigations have been completed and a number of new ones initiated. Included are processes involving only mechanical separation and processes combining chemical flocculation and mechanical separation.

MICROSCREENING

Principle of Operation

Microscreening is a form of simple filtration. The minimum particle size removed depends upon screen mesh size and pattern of weave. Because of the layer of material that collects on the screen during use, the minimum particle size is actually somewhat less than the size of the screen openings.

Experimental Investigation

An investigation was made using a Microstrainer* to filter Lebanon, Ohio, secondary effluent (1). This particular device, shown in Figure 1, uses a screen in the form of a partly submerged rotating drum or cylinder. Water flows continuously by gravity through the submerged portion from inside the drum to a clear-water storage chamber outside the drum. Because of the rotation of the

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**Equipment loaned by Glenfield & Kennedy, Inc., King of Prussia, Pa.*

drum, the filtering portion is constantly renewed to maintain a practical filtration rate and the former filtering portion is raised above the water for cleaning. Cleaning is carried out by backwashing with sprays of product water. Backwash requirement is 5 percent or less of the feed volume. An ultraviolet light is used to control growths on the screen.

The drum of the unit tested was 5 ft in diameter and 1 ft in width. This gave about 15 ft^2 of screen surface of which about 9 ft^2 was submerged. With this unit it was possible to treat up to about 60 gpm when suspended solids were low. Since pressure-drop rather than flow rate was controlled, the flow rate was not constant. Flow rate is greatly affected by the amount of suspended solids.

Suspended solids, BOD, total organic carbon (TOC) and turbidity-removal data were taken using two types of screens, one having 23 micron openings and one having 35 micron openings. The average removals are shown in Table 1.

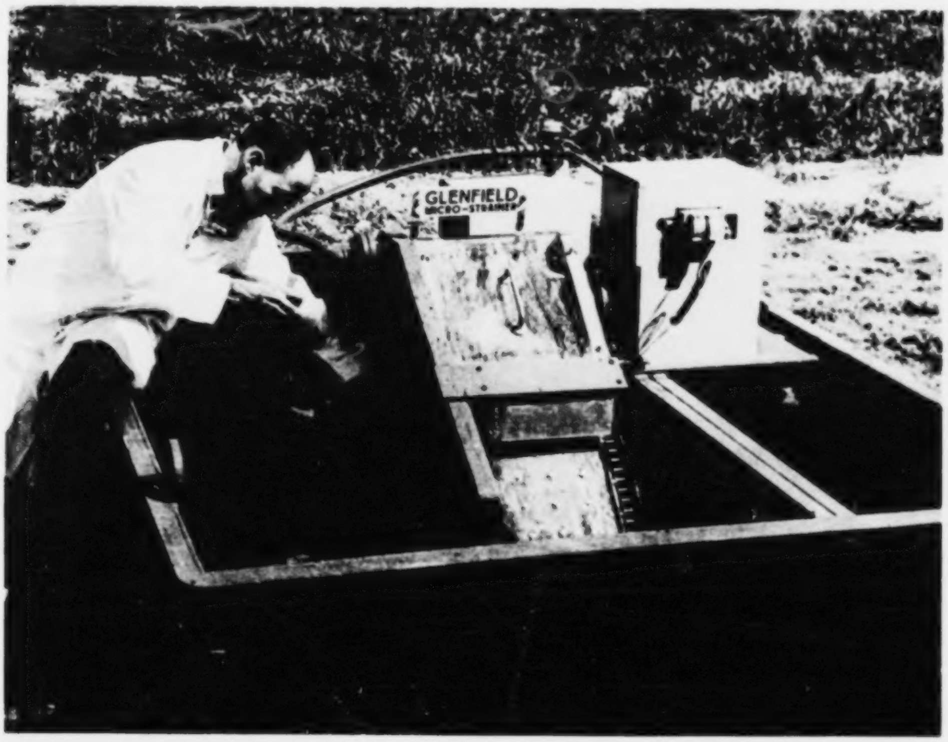

Figure 1. Pilot microscreening equipment at Lebanon, Ohio. Wastewater enters the compartment on the left and flows by gravity radially outward through the rotating drum screen in the center to the compartment on the right. At the top of the drum, streams of product water are pumped downward on the screen to backwash solids off. The backwash stream is taken off as waste. Here a sample of backwash water is being taken for analysis.

Table 1. AVERAGE CONTAMINANT REMOVALS OBTAINED WITH A MICROSTRAINER

Screen Openings (microns)	Percent Removal			
	Suspended Solids	Biochemical Oxygen Demand	Total Organic Carbon	Turbidity
23	89	81	30	76
35	73	61	30	60

Although the finer screen has the better removal capability, as one would expect, both screens remove a considerable amount of the suspended solids. The high degree of BOD removal shows that most of the biodegradable material was insoluble. TOC measurements are subject to considerable error when suspended material is present, but these results show roughly what gross organic removal might be expected.

Cost estimates were made for treating secondary effluent by microscreening. For a 10-mgd plant the total operating cost, including amortization of equipment, should be about 1.5 /1,000 gal. The type of screen will have only a small effect on cost.

DIATOMACEOUS EARTH FILTRATION

Principle of Operation

Diatomaceous Earth (DE) filtration is a form of mechanical separation that uses a layer of powdered filter aid, diatomaceous earth, built up on a relatively loose septum to screen out the suspended solids. As filtration proceeds, the filter-aid layer will become clogged with deposited solids. To prevent a rapid build-up of pressure, more filter aid must continuously be added to the feed so that a porous cake is produced. This filter aid is called body feed. Eventually the pressure becomes too great to continue operation. At that time, the filter must be backwashed and a new precoat applied.

The minimum size particle that can be removed is related to the size of openings between filter-aid particles which, in turn, is related to the particle size of the filter aid. Since pressure drop increases as filter-aid particle size decreases, there is a practical lower limit. Generally, the minimum size particle that can reasonably be removed is about 0.5 to 1.0μ. By changing the zeta potential of the filter aid through treatment with alum or certain polyelectrolytes, it is possible to improve somewhat the removal capability.

Experimental Investigations

Pomona Pilot Scale Work - A study of diatomaceous earth filtration was made at the Pomona Research Facility. Both a vacuum filter and a pressure filter were tested. The vacuum filter had 8 flat-leaf septa, vertically suspended and covered with polypropylene filter cloth. Filter area was 120 ft.^{2} The pressure filter also had vertical filter leaves. The filter area was 180 ft.^{2}

Data were obtained on both filters while filtering secondary effluent over a range of filter rates, body-feed concentrations, and filter-aid types. Although each filter-aid type used has a wide range of particle sizes, the manufacturer* indicates that 50 percent by weight will be less than 31 microns for Celite 545, 15 microns for Celite 503, 11 microns for Hyflo Super-Cel and 7 microns for Standard Super-Cel.

Results for the vacuum-filter tests are shown in Table 2. These results indicate the run-length that might be expected for a given set of conditions. As one would expect, longest runs were obtained with the coarsest grade filter aid. Unusually short runs were obtained with Celite 503 because of the low ratio of body feed to turbidity. Turbidity removal for all runs averaged roughly 85 percent. Data from runs not shown in Table 2 indicated for Celite 545 at 0.52 gpm/ft ^{2} a chemical oxygen demand (COD) decrease of about 21 percent.

Estimation of the minimum cost of diatomaceous earth filtration requires optimization with respect to body feed and flow rate. A rough estimate of

Table 2. VACUUM DIATOMACEOUS EARTH FILTRATION OF SECONDARY EFFLUENT

Flow Rate (gpm/ft^2)	Filter Aid	Body-feed Conc. (mg/l)	No. of Runs	Run-length (hrs)	Turbidities (JTU)* Feed	Product
0.53	Celite 545	42	5	19.6	5.5	0.8
0.75		33	3	10.7	5.2	0.8
1.0		19	1	5.4	4.4	0.4
0.51	Celite 503	36	2	6.0	10.5	3.3
0.75		29	1	3.0	9.2	0.7
1.0		21	1	1.2	8.0	0.75
0.54	Hyflo	35	6	12.7	4.6	0.85
0.75	Super-Cel	21	2	4.4	5.8	0.8

Precoat - 0.1 lb/ft^2

Headloss at end of run - 18 in.Hg

*Jackson Turbidity Units

**Johns-Manville Products Corp., New York, N.Y.*

5¢/1000 gal. for a 1-mgd plant has been made, however, for vacuum filtration at 0.5 gpm/ft.^{2} using Celite 545. This figure does not include cost of disposal of sludge nor does it consider recovery of filter aid from the sludge. For large installations, filter-aid recovery might provide a significant saving.

Pressure filter results are shown in Table 3. Run-lengths are generally longer than for the vacuum filter, primarily because it is possible to operate to considerably higher pressure drops. Turbidity removal was poor compared to the vacuum filter. The reason for the difference is not definitely known. Organic and biological removals were checked on some runs. COD reduction of about 13 percent was observed using Celite 545. For the same filter aid, average coliform reductions of about 44 percent and total bacteria reductions of about 83 percent were observed. Hyflo Super-Cel gave a coliform reduction of 53 percent and total bacteria reduction of 69 percent. Although the biological results must be considered to show only very approximately the removals that may be expected, they do demonstrate clearly that significant numbers of bacteria will remain after diatomaceous earth filtration.

The cost of pressure filtration is estimated to be very nearly the same as for vacuum filtration. Although the capital cost is greater for pressure filters, the longer runs that can be obtained compensate for the difference.

Some work was done with the vacuum filter on secondary effluent that had first been passed through granular activated carbon. Although the primary purpose of the granular carbon is to remove soluble organic materials, it also acts as a filter for the larger suspended solids in the secondary effluent. As a result,

Table 3. PRESSURE DIATOMACEOUS EARTH FILTRATION OF SECONDARY EFFLUENT

Flow Rate (gpm/ft^2)	Filter Aid	Body-feed Conc. (mg/l)	No. of Runs	Run-length (hr)	Turbidities (JTU)* Feed	Turbidities (JTU)* Product
0.50	Celite 545	50	1	>50.0	8.2	3.1
0.75		19	2	24.2	5.7	2.5
0.81		42	2	28.4	8.3	3.9
1.0		20	2	7.3	6.4	2.1
1.0		45	3	31	7.5	3.0
0.76	Celite 503	18	1	14.5	7.0	4.0
0.78	Hyflo Super-Cel	21	1	22.3	8.1	4.9
1.2		29	1	9.7	6.5	3.8

Precoat - 0.1 lb/ft^2

Head loss at end of run - 35 psi

*Jackson Turbidity Units

carbon-treated effluent has very low turbidity. Filtration results are shown in Table 4. Because of the low feed turbidity, no body feed was used. Run-lengths were considerably greater than for untreated secondary effluents. Flow rates up to 2 gpm/ft.^{2} appear practical. Turbidity removals were, with one exception, less than 50 percent. The carbon treatment apparently removes much of the larger particle size turbidity, leaving a large fraction of material that is not removed by the filter aids commonly used for water. Bacterial removals were also poor. Celite 545 showed almost no removal of bacteria. Data from one run, using Hyflo Super Cel, showed 60-percent removal of coliforms and 43-percent removal of total bacteria. Because of the small consumption of filter aid and the high filtration rates that can be used, the cost of filtering carbon column effluent should only be 1.5 to 2¢/1000 gal including amortization.

Lebanon Pilot Operation - Although a detailed study has not been made, some operating data were obtained on a pressure filter producing water for an electrodialysis study at the Lebanon, Ohio Advanced Waste-Treatment Pilot Plant. The filter had 96 ft ^{2} of filtering area and was operated at a rate of about 0.7 gpm/ft ^{2} to a maximum pressure drop of 16 psi. The filter aid was Celite 503 that had been treated with 7.5 percent-by-weight alum and neutralized with soda ash. The secondary effluent suspended solids concentration was usually slightly higher and more variable than at Pomona. As a result, a higher body-feed concentration was required. To allow a margin of safety for upswings in turbidity, a body feed of 80 to 100 mg/l was usually employed. Occasionally, runs of more than 30 hours were observed; runs were frequently between 4 and 8-hrs duration.

Table 4. VACUUM DIATOMACEOUS EARTH FILTRATION OF CARBON COLUMN EFFLUENT

Flow Rate (gpm/ft^2)	Filter-aid	No. of Runs	Run-length (hrs)	Turbidities (JTU)* Feed	Turbidities (JTU)* Product
1.5	Celite 545	3	33	1.11	0.72
2.0		2	31	1.24	0.77
1.0	Hyflo	3	22	0.80	0.41
1.5	Super-Cel	3	15	0.43	0.21
1.0	Standard Super-Cel	1	10	1.05	0.65

Precoat - 0.1 lb/ft^2

Body feed - none

Headloss at end of run - 18 in.Hg

*Jackson Turbidity Units

The product turbidity was found to vary with water temperature. In the winter, with water temperatures as low as 11° C, the product water usually had a turbidity of about 1 JTU. In the summer, at temperatures near 25° C, product turbidities were usually 0.1 JTU or less. The reason for this variation is not clear, but is probably related to differences in the biological treatment.

Because of the greater consumption of filter aid at Lebanon, the cost of treatment would be several cents per 1,000 gal. higher than estimated from Pomona results.

CHEMICAL CLARIFICATION

Principle of Operation

Chemical clarification usually includes a coagulation step, a flocculation step, a sedimentation step, and a filtration step. Coagulation or destablization of colloidal suspensions is achieved by addition of chemicals which are rapidly mixed with the water. The formation of small floc particles results. Further slow stirring allows floc particle size to increase by agglomeration. This is the flocculation step. Usually the floc is at least partly composed of a hydrous oxide that has a slight positive charge. Metals whose oxides are involved are usually aluminum, iron, or in the case of lime treatment, magnesium. The floc particles have ability to aggregate colloidal particles and adsorb or entrap them. The mechanisms involved are not completely known. There is a lowering of the usually negative zeta potential of the colloidal particles that would tend to destablize colloidal dispersion. There is also an attraction between the slightly negatively charged colloid particles and the slightly positive floc particles. The result, when proper chemical doses are used, is a very effective tying-up of suspended solids into floc particles, most of which are large enough to settle well.

Most of the flocculated material is removed by sedimentation. The water is allowed to flow slowly enough through a basin that gravity settling occurs. In some cases, water of good clarity can be obtained by settling alone. Usually, however, further removal of floc particles by filtration is necessary.

Filtration of chemically clarified water is usually carried out in beds of porous media such as sand or coal. A combination of straining, sedimentation, and further flocculation in the filter contributes to removal of most of the floc remaining after the sedimentation step. In the most common type of filter, the sand filter, much of the removal is by straining at the sand surface. As the floc layer builds up, pressure drop over the filter increases. When the pressure drop reaches a predetermined value, feed-water flow is stopped and clear water is passed backward through the filter at a high enough rate to fluidize the sand and remove the collected floc. If a larger-size medium is used so that the floc can penetrate some distance into the filter, the other mechanisms become more important. Because floc retention occurs in the volume of the filter rather than just near the surface, the pressure-drop build-up is slowed and run-lengths increased. By constructing the filter of two or more layers with each layer having a smaller particle size than the one above, and with the top layer of sufficient particle size that little straining occurs, it is possible to take advantage of all three mechanisms. Filters built in this manner are called multi-media filters and are sometimes used to carry out all three steps of the clarification process. Coagulating chemicals are mixed with water, which is immediately applied to the filter. Although floc size is initially too small for much removal to occur at the filter surface, the size increases sufficiently during passage of the water through the filter that the suspened solids are effectively strained out and stored in the interstices of the media.

When lime is used in chemical treatment,softening or removal of calcium and magnesium occurs along with clarification. Lime adds hydroxyl ion to the water that reacts with bicarbonate ion, forming carbonate ion. Calcium is then precipitated as calcium carbonate. The degree of calcium removal depends on pH and is maximized at a pH of about 10. If the pH is further increased to about 11 with additional lime, magnesium precipitates as magnesium hydroxide. At this pH there is not sufficient carbonate to precipitate all the calcium added with the lime. Additional carbonate must be added in one of several ways. When this is done, the pH is again reduced to about 10. Operation for both magnesium and calcium removal requires two separate reaction chambers and is referred to as two-stage treatment. Partial softening obtained by raising the pH high enough for only calcium removal is one-stage streatment.

The sludge from a lime clarifier contains a large fraction of calcium carbonate. This material forms a crystalline precipitate that can be carried out the overflow weir of a settler unless the particle size is sufficiently large to hasten settling. To increase particle size,it is common practice to recirculate sludge back into the part of the clarification system where new floc is being formed. This is referred to as solids-contact operation. It may be carried out by pumping settled sludge back into the clarifier or by designing the equipment so that some of the sludge in internally recirculated. Various designs are available from manufacturers of clarification equipment that make use of solids-contact.

Experimental Investigations

Laboratory Studies - Initial studies of the effectiveness of chemical clarification are usually made using jar tests. These are breaker-scale batch tests. Chemicals are added to a beaker of water, the water is stirred rapidly for several minutes and then more slowly for 15 to 30 minutes to allow flocculation to occur. The flocculated material is then allowed to settle. The clarity and other characteristics of the supernatant liquid can be observed with or without filtration. These tests give an indication of the chemical doeses and some of the conditions that will be required to obtain good clarification in larger-scale equipment.

Jar tests were conducted on wastewaters from a number of locations before considering work on larger-scale equipment. Generally these tests show that both poorly and well-treated secondary effluent can be chemically treated with lime or alum to give turbidities of less than 1 JTU after filtration. Alum doses as low as 150 mg/l and lime doses as low as 50 mg/l have been used to achieve that turbidity level. A somewhat higher dose for lime would, however, probably be used in most cases to achieve removal of certain pollutants besides suspended materials.

Clarification Pilot Plant Studies - Several pilot-scale investigations have been undertaken. The most extensive of these is being carried out at the Lebanon Pilot Plant (2). The equipment shown in Figures 2 and 3 is used to study a range of operating variables affecting coagulation, flocculation, settling, and filtration. It is also possible to bypass the flocculator and settler for study of the mode of operation in which flocculation occurs in the filter itself. Three types of filters are included: anthracite coal, sand, and dual-media consisting of coal over sand. Filter-media characteristics are shown in Table 5. Feed and

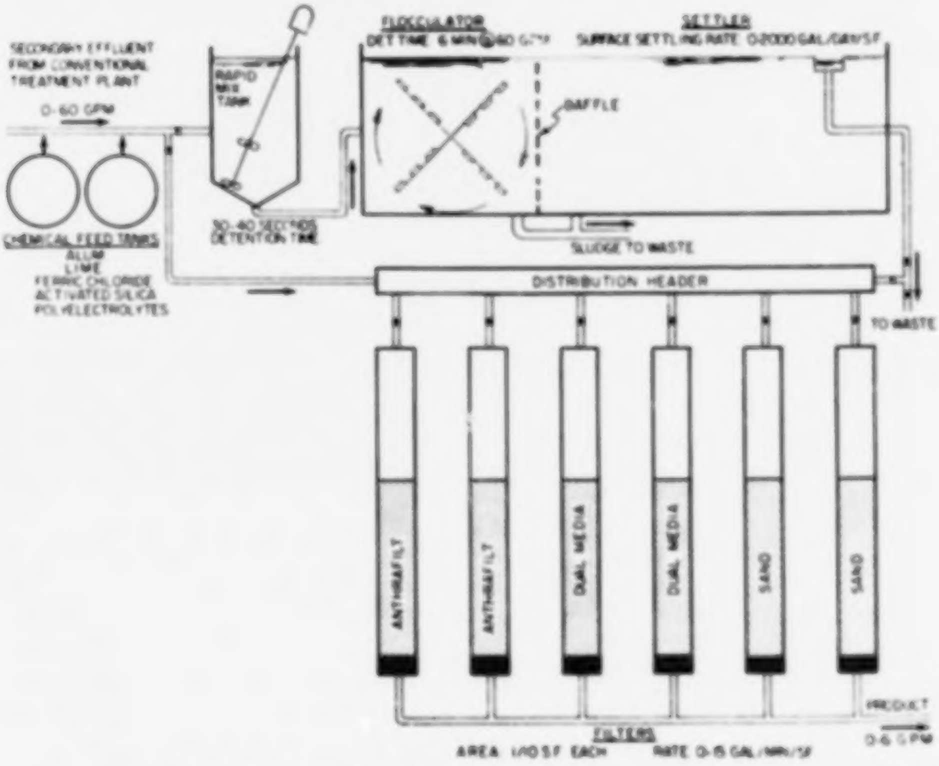
FLOCCULATOR
DET TIME 6 MIN @ 60 GPM
SETTLER
SURFACE SETTLING RATE 0-2000 GAL/DAY/SF
SECONDARY EFFLUENT
FROM CONVENTIONAL
TREATMENT PLANT
0-60 GPM
RAPID
MIX
TANK
BAFFLE
30-40 SECONDS
DETENTION TIME
SLUDGE TO WASTE
CHEMICAL FEED TANKS
ALUM
LIME
FERRIC CHLORIDE
ACTIVATED SILICA
POLYELECTROLYTES
DISTRIBUTION HEADER
TO WASTE
ANTHRAFILT
ANTHRAFILT
DUAL MEDIA
DUAL MEDIA
SAND
SAND
PRODUCT
0-6 GPM
FILTERS
AREA 1/10 SF EACH
RATE 0-6 GAL/MIN/SF

Figure 2. Suspended solids removal study, Lebanon, Ohio

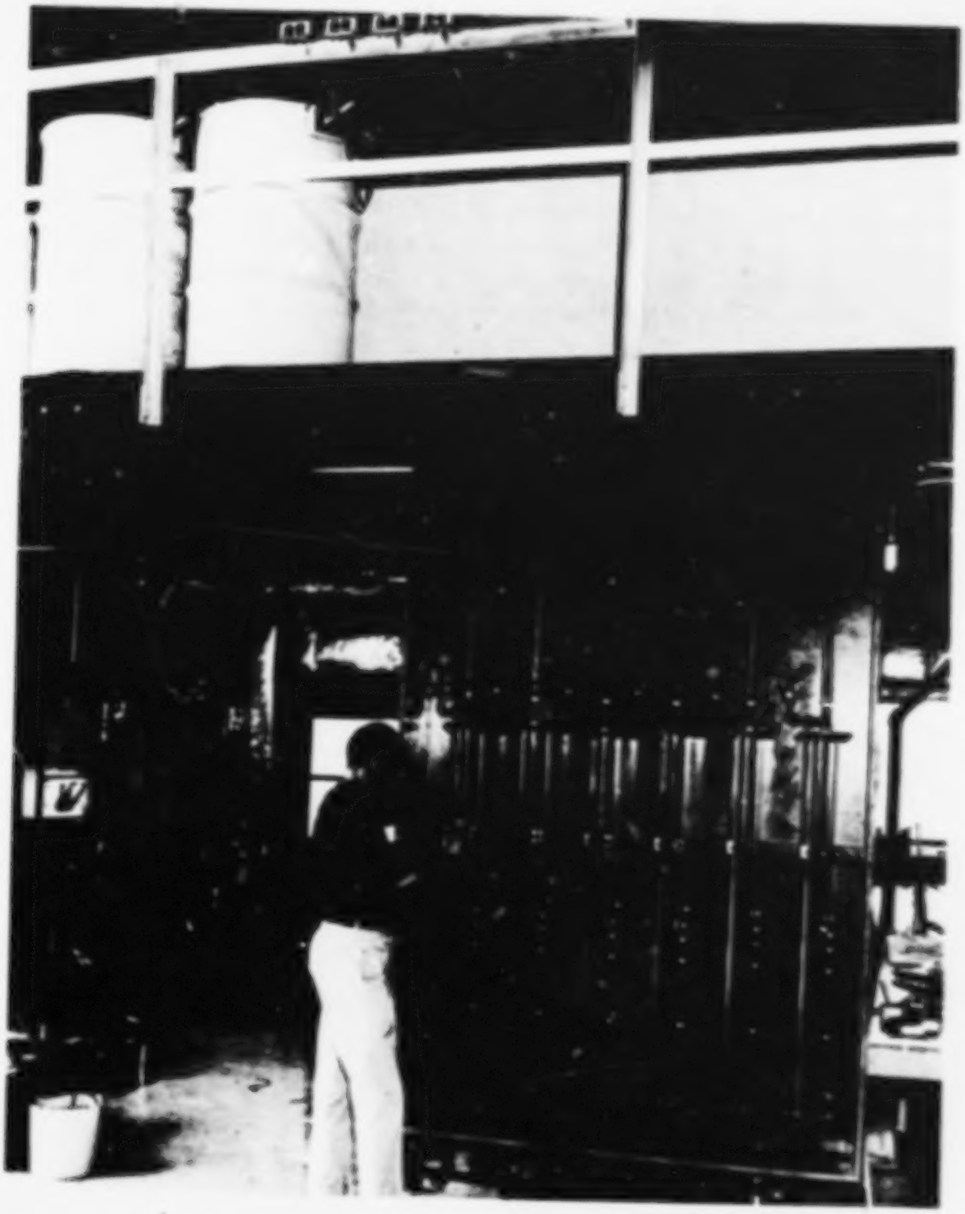

Figure 3. Solids removal study at Lebanon, Ohio. At the top of the picture are containers for holding and mixing of coagulating chemicals. Behind the containers are a flocculator and settler. Efficiency of suspended solids removal can be investigated for different chemicals over a range of chemical doses, flocculator speeds, and settler flow rates. At the bottom are six filters that receive water from the settler. Various filter media can be tested for pressure drop characteristics and solids removal capability over a wide range of flow rates. Taps in the walls of the filters are for measuring pressures down through the filter bed.

Table 5. FILTER MEDIA CHARACTERIZATION DATA

Filter	Depth (inches)	Effective Size (mm)	Uniformity Coefficient	Porosity (%)
Single Medium				
Sand	24	0.45	1.33	40
Coal	24	0.75	1.50	50
Dual Media				
Sand	6	0.45	1.33	40
Coal	18	0.90	1.75	50

product turbidities are automatically monitored and recorded. Pressures at various points in the filters are also automatically recorded.

The use of alum as a flocculant has been studied in detail, both alone and with activated silica as a floc strengthener. During this work, the flow rate through the settler was varied from 300 to 900 gpd/ft^2 and the alum dose was varied from 0 to 500 mg/1. Filters were usually operated at 3 gpm/ft.^{2}

Some typical run-length results for dual-media filters using alum alone are shown in Figure 4. All runs involved were terminated when product turbidity reached 1.0 JTU. The results give an idea of the maximum run-lengths and the chemical dose at the maximum that might be expected for the stated conditions. Similar relationships were found for the filters using coal alone. Because of the polishing effect of the sand at the bottom of the dual-media filters, these filters generally gave better product quality than just coal. It is obvious from the two plots in Figure 4 that the conditions in the flocculator-settler have a large effect on filtration results. An increase in settler overflow rate increases the amount of floc in the filter feed and decreases filter run-length. The amount of alum required for maximum run-length was, however, roughly cut in half at the higher settler rate. For the conditions investigated, the net production of the dual-media filters was 34 to 214 gal/ft of headloss. Backwash water ranged from 2 to 20 percent of the feed. Similar results were obtained in the coal filters.

The use of activated silica along with the alum decreased the tendency for turbidity breakthrough and increased the length of filter run for the dual-media filters. Using 2 mg/1 of silica, the lowest dose tested, the average length of filter run was almost 3 times that without silica. For this silica dose, some runs reached the maximum operating head loss of 8 ft of water and had to be terminated before the 1-JTU turbidity criterion was exceeded. Above 2 mg/1 of

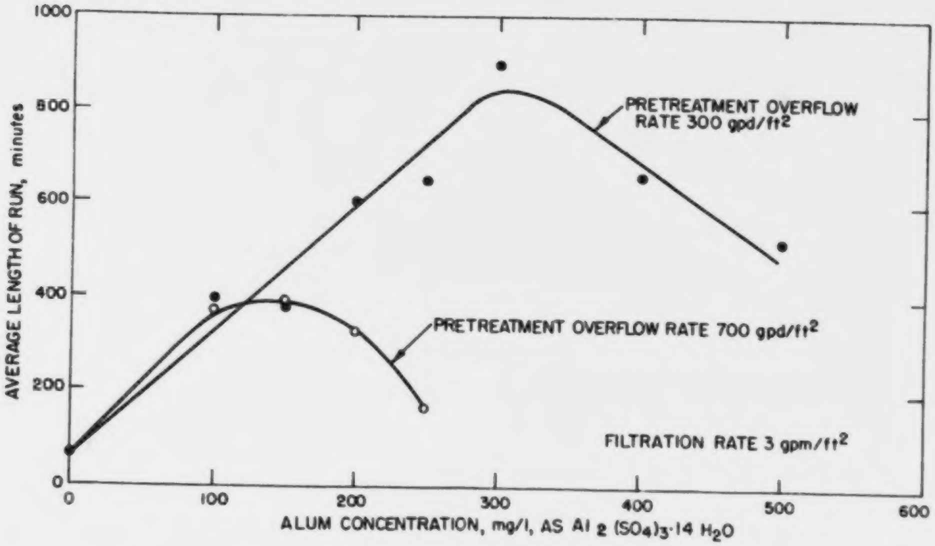

Figure 4. Effect of alum dosage on length of run for dual media filters.

silica, the fraction of runs terminated by headloss increased as silica dose increased. The average run length decreased.

For a 1-JTU turbidity criterion, the 0.9-mm coal and the 3-gpm/ft ^{2} filtration rate initially chosen for dual-media-filter tests do not give maximum water production per filter run when silica is used to strengthen the floc. Study of other coal sizes indicates that filter production can be increased by increasing coal size to about 1.1 or 1.2 mm. Investigation of filtration rates of 3, 4, and 5 gpm/ft ^{2} showed that 4 gpm/ft ^{2} gives maximum production per filter run. This was found to hold over a coal particle-size range from 0.9 to 1.8 mm.

Correlation of run-length with alum dose was not possible for the sand filters. There was, however, a more definite relationship between solids load to the filter and run-length than for the dual-media and coal filters. This relation is shown in Figure 5. Even without the use of silica, sand-filter runs were terminated at a head-loss of 8 ft of water rather than by turbidity breakthrough as in the case of the other two types of filters. At 8 ft of head, turbidity was consistently less than 1 JTU. Net production from the sand filters ranged from 4 to 54 gal/ft of head-loss. Backwash requirements were from 3 to 28 percent of the feed.

Pressure readings taken at various points in the filters showed that good distribution of floc throughout the filter volume took place in the coal and dual-media filters. For the sand filters, most of the pressure-drop took place in the first few inches as expected.

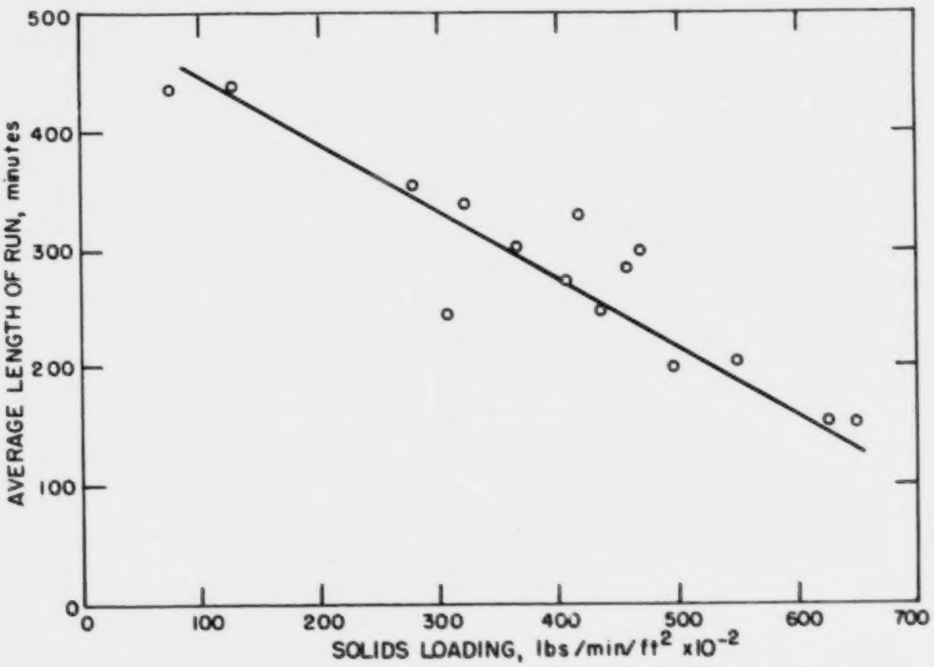

Figure 5. Effect of solids loading on sand filter performance at 3gpm/ft.^{2}

An important aspect of clarification processes, especially when dealing with wastewater, is the degree of removal of microorganisms. Table 6 shows bacterial-count data for some pilot runs. Removal for all types of filters was excellent.

A tentative cost estimate for alum treatment of secondary effluent in a 10-mgd plant has been made. Using a settler overflow rate of 700 gpd/ft ^{2} and an alum dose of 150 mg/1, the cost should be about 5¢/1,000 gal. If it were desired to add enough alum to obtain 95 percent phosphate removal, about 300 mg/1, the cost would increase to about 8¢/1,000 gal.

Pressure Coal Filter - A short-term investigation was made of a pressure filter.* The equipment is shown in Figure 6. The filter is designed to use anthracite coal, Number 1.5 Anthrafilt,** as a filter medium and to operate at a very high rate of 10 gpm/ft ^{2} up to a pressure of about 25 in. Hg. Essentially no flocculation time is provided and there is no settler. Instead, floc is retained in the filter bed. During the study, 20 in. of coal and 14 in. coal underlaid by 6 in. of 0.45 mm sand, were used in the filter. Under the filter media there was a bed

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**Equipment loaned by Zurn Industries, Inc., Erie, Pa.*

***Palmer Filter Equipment Co., Erie, Pa.*

Table 6. BACTERIAL REMOVAL FROM SECONDARY EFFLUENT BY CHEMICAL COAGULATION AND FILTRATION

Sample Stream	Secondary Effluent	Settled Product	Filter Product Coal	 Dual-Media	 Sand
Average Total Plate - counts per 100 ml	72×10^6	8.0×10^5	2.2×10^5	2.6×10^5	2.3×10^5
Average Fecal Streptococcus - counts per 100 ml	7.5×10^3	200	29	7	2

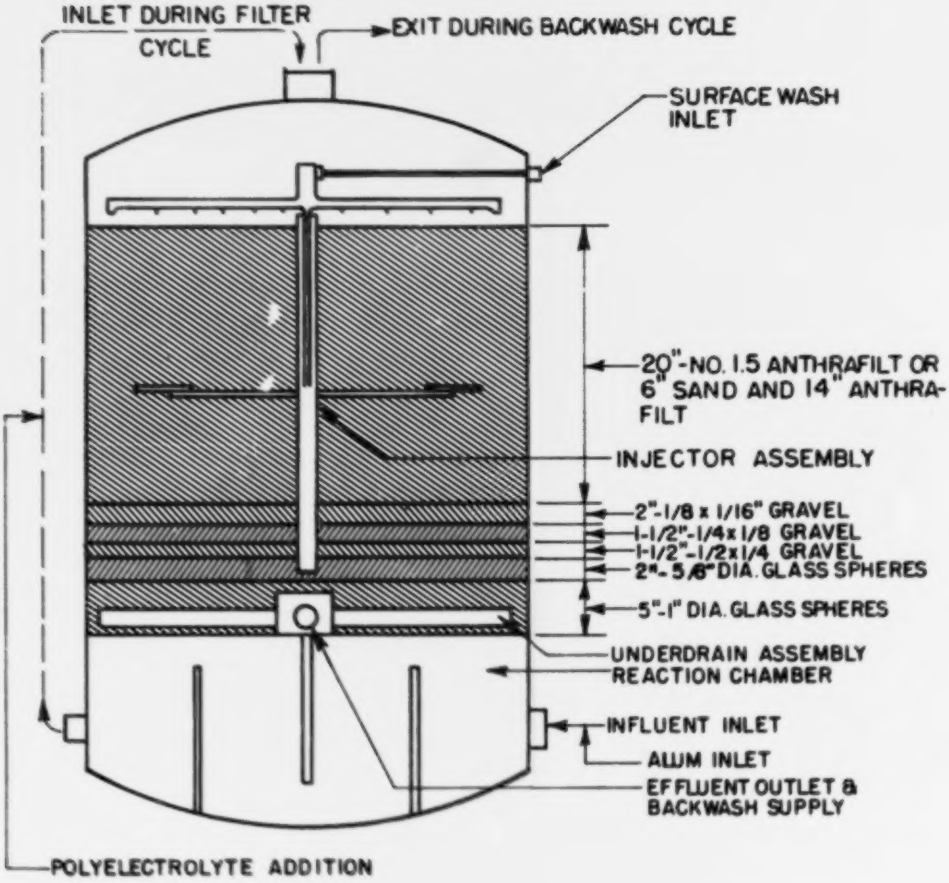
INLET DURING FILTER CYCLE
EXIT DURING BACKWASH CYCLE
SURFACE WASH INLET
20"-NO. 1.5 ANTHRAFILT OR 6" SAND AND 14" ANTHRAFILT
INJECTOR ASSEMBLY
2"-1/8 x 1/16" GRAVEL
1-1/2"-1/4 x 1/8 GRAVEL
1-1/2"-1/2 x 1/4 GRAVEL
2"-5/8" DIA. GLASS SPHERES
5"-1" DIA. GLASS SPHERES
UNDERDRAIN ASSEMBLY
REACTION CHAMBER
INFLUENT INLET
ALUM INLET
EFFLUENT OUTLET & BACKWASH SUPPLY
POLYELECTROLYTE ADDITION

Figure 6. Schematic arrangement of pressure filter unit.

of graded gravel. Rates of 5 gpm/ft ^{2} and 10 gpm/ft ^{2} were investigated. Most of the work was done with 10 to 15 mg/l alum as the flocculant and up to about 2.5 mg/l of a cationic polyelectroyte Primafloc C-7,*** as a flocculant aid. Another cationic, one anionic, and one nonionic polyelectrolyte were tested, but did not give as good product quality as the C-7.

Some typical data using coal alone in the filter and a rate of 10 gpm/ft ^{2} are shown in Figure 7. It is quite obvious that the polyelectrolyte significantly improves product quality. This is considered to result from a strengthening of the floc. The improvement in product quality is obtained at the expense of a higher rate of pressure build-up. Reducing the flow rate to 5 gpm/ft ^{2} roughly doubled the length of filter run, based on 25 in. Hg pressure drop as the cutoff point. The average run-length at 10 gpm/ft ^{2} was about 2.5 hours.

The filter was run using dual media to see if the amount of polyelectrolyte could be decreased. It was felt that the fine particle size of the sand should prevent turbidity breakthrough with a weaker floc than for the case of coal alone. Surprisingly, it was not possible to reduce the polyelectrolyte dose much below 2.5 mg/l without getting breakthrough. At similar chemical doses, the average run-length for the dual-media filter did not appear to be greatly different from the filter using only coal.

Because of the short filter runs compared to operation with a flocculator and settler, backwash requirements were high. For a 2.5-hr run, 6.6 percent of the feed was required; for a 1.5-hr run, 11 percent was required. Mudball formation was a problem.

Total cost of operating a 1-mgd plant, including amortization of equipment, is estimated at about 7¢/1,000 gal. This is based on a 10-gpm/ft^2 rate and polyelectrolyte and alum dose of 2.5 and 11 mg/l. The cost could be reduced significantly if the dose of polyelectrolyte could be reduced.

Lime Clarification Pilot Plant Studies - A 75-gpm, single-stage, lime-clarification system has been installed at the Lebanon Pilot Plant. The primary purpose of the system is to supply clarified water for other pilot plant studies using secondary effluent for feed. The equipment is shown in Figure 8. It consists of an upflow solids-contact type flocculator-settler combination and two dual-media filters in parallel. Sludge from the settler is gravity thickened to about 10 percent solids by weight and conveyed to drying beds.

Figure 9 shows the interior of the clarifier. Feed water and lime are mixed in the innermost compartment. This compartment contains a dilute slurry of

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****Rohm & Haas Co., Philadelphia, Pa.*

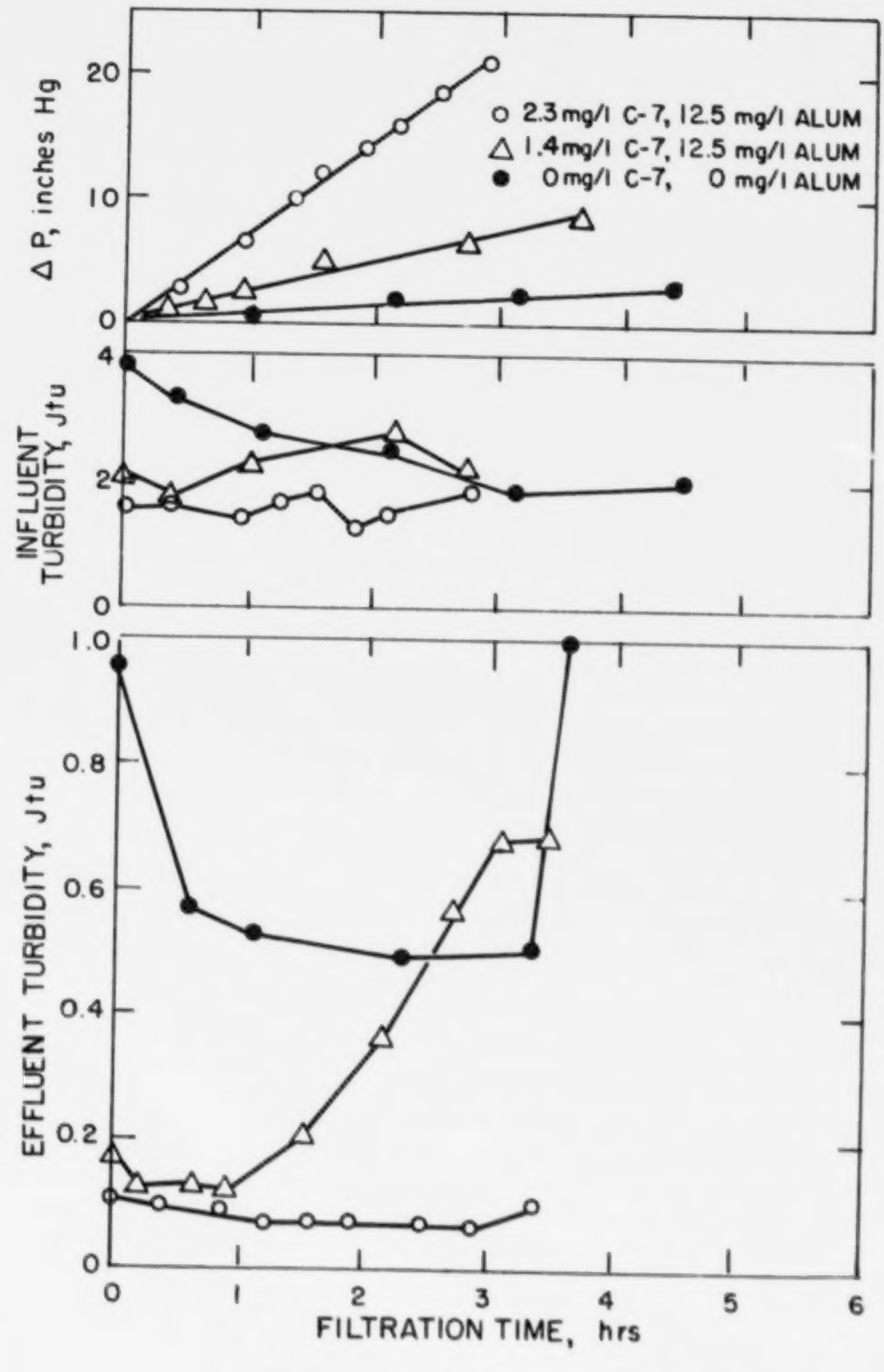

Figure 7. Pressure coal filter results.

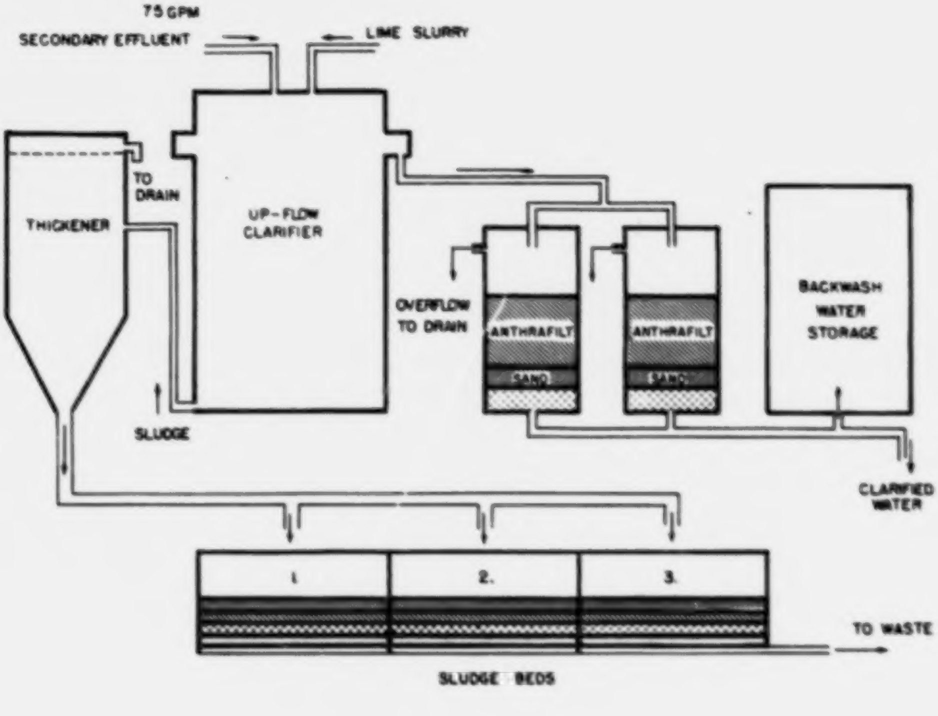
75 GPM
SECONDARY EFFLUENT
LIME SLURRY
TO DRAIN
THICKENER
UP-FLOW CLARIFIER
OVERFLOW TO DRAIN
ANTHRAFILT
ANTHRAFILT
SAND
SAND
BACKWASH WATER STORAGE
SLUDGE
CLARIFIED WATER
1
2.
3.
TO WASTE
SLUDGE BEDS

Figure 8. Lime clarification system at Lebanon Pilot Plant.

sludge that is continuously being pumped up from the bottom of the clarifier by an agitator. Calcium carbonate and other precipitates begin to form using the sludge particles as "seeds" (solids-contact). The water then flows downward in the space between the inner cylinder and the cone where particle size of the suspended material increases. Most of the solids settle out; others are carried a short distance up with the water in the outer compartment forming a sludge blanket. This blanket helps trap small particles and allows them to agglomerate to settleable size. The water travels upward and out through a ring of holes near the top of the clarifier. Upflow rate at the water surface is 1 gpm/ft ^{2} A water-pulse system is used to move sludge out to a sludge collector ring. A scraping mechanism could be used equally well. Sludge is removed from the clarifier as a 1- to 2-percent slurry. The height of the sludge blanket can be controlled to some degree by the rate of sludge removal.

The dual media filters contain a 6-in. layer of sand overlaid by an 18-in. layer of anthracite coal. The sand has a particle size range of 0.45 to 0.55 mm. The coal is No. 1 Anthrafilt.*

**Palmer Filter Equipment Co., Erie, Pa.*

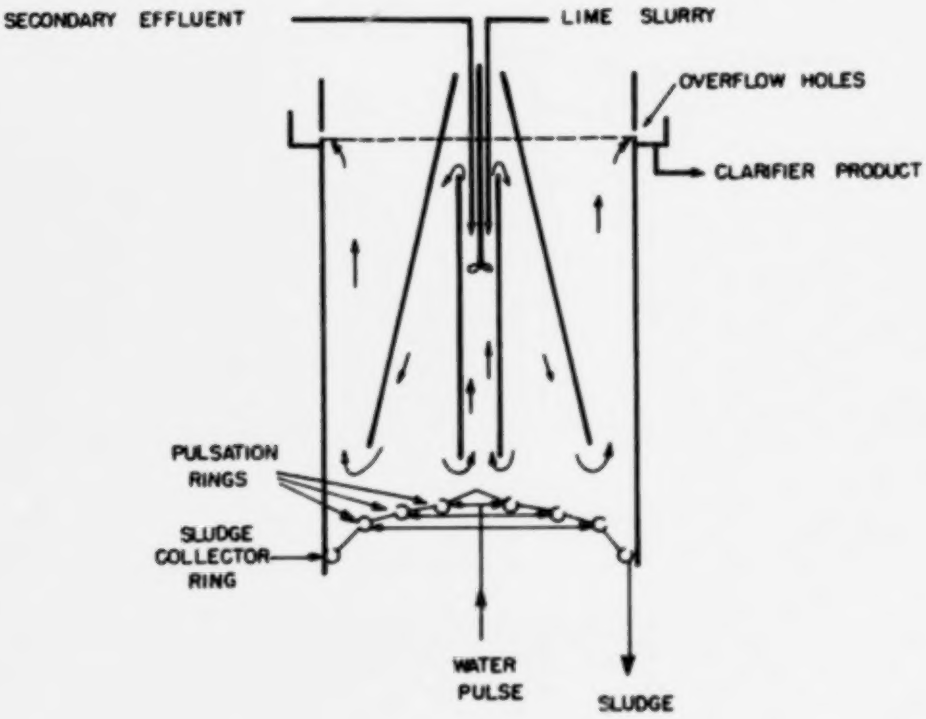
SECONDARY EFFLUENT
LIME SLURRY
OVERFLOW HOLES
CLARIFIER PRODUCT
PULSATION RINGS
SLUDGE COLLECTOR RING
WATER PULSE
SLUDGE

Figure 9. Details of lime clarifier at Lebanon Pilot Plant.

It is intended that the clarification system will be run at the lowest pH that will provide high clarity water. Preliminary results with secondary effluent indicate that a pH of 9.5 will produce water of less than 0.5-JTU turbidity from the filters without use of a flocculant aid. At this pH, phosphate is reduced to about 3 mg/l or less as PO_4. Calcium is reduced from about 100 mg/l to about 50 mg/l, but there is no reduction in magnesium concentration. A small amount of data at pH values above 9.5 indicate improved phosphate removal.

Future Work

Extensive work on chemical clarification is planned. At the Lebanon Pilot Plant, data will be obtained on the recently installed lime clarrification unit. A limited study of removals of turbidity, calcium, magnesium, alkalinity, and phosphate from secondary effluent will be made at pH values up to 11 when the equipment is not needed for production of clarified water at lower pH. Lime consumption will be measured and related to pH and water composition. Study of primary effluent is also planned.

Further study will be made of alum treatment with emphasis on methods to recover aluminum for reuse. Aluminum recovery improves the economics of alum treatment by reducing chemical cost and sludge disposal cost.

A 5-gpm, two-stage lime clarifier has been installed at the Pomona Research Facility. It is of the solids-contact type. The purpose of the equipment is to supply clarified water to a small carbon and ion exchange treatment system. Clarification and softening data will be obtained.

At the Washington, D.C. Pilot Plant, a 70-gpm, two-stage lime clarification system is being installed. It is also solids-contact equipment. Product water will be used in other treatment processes. A multiple-hearth furnace is also being installed in which calcium carbonate from the clarifier sludge will be recalcined to recover lime. Lime recovery is practiced in softening of well waters, but has not been applied to wastewater treatment.

ORGANIC REMOVAL

Although the biological sewage treatment methods are used primarily to remove organic materials from wastewater, they are not capable of removing the last traces of these materials. Besides suspended solids, there remain measurable amounts of refractory soluble organics, or more accurately, materials not removed by clarification. It is the removal of these organic materials that we are concerned with here. The composition of these materials is largely unknown. Certain classes of materials have been identified, but a complete analysis has not and may never be made. Although not easily biologically oxidizable, the soluble organics do exercise an oxygen demand in a receiving stream. This in itself is a good reason for removing them, especially when a large fraction of the stream flow is of wastewater origin and has a low dissolved oxygen content. When traces of certain synthetic or industrial wastes are present, fish and other animal life can be killed, weakened, or at least made unfit for human consumption. When the wastewater is to be reused for human consumption, either by direct recycle or after dilution in a receiving stream that is largely of wastewater origin, the organics must be removed to prevent taste, odor, and color. Although the toxicological effect on humans has not been established, removal of the organics would be the only safe way to assure against long-term health effects.

While a high degree of removal of soluble organics is desirable for direct reuse of wastewater, lesser removal when there is a very large amount of dilution water or removal of only certain contaminants might be all that is necessary. Processes for organic removal do not, therefore, always have to remove a large fraction of the gross organics. Partial and selective processes also may be of value.

ADSORPTION ON GRANULAR ACTIVATED CARBON

Principle of Operation

Many solids have the ability to attract to their surface soluble materials from solution. The phenomenon is called adsorption. By giving a solid a very porous structure, a very large surface per unit volume results. Certain porous solids are, therefore, excellent adsorbents.

Activated carbon is a porous material having a high adsorption capacity for the soluble organics in wastewater. This material can be contacted with the water either as a fine powder or as granules having a particle size usually in the range of 8 to 40 mesh. The use of granular carbon has been found convenient in treatment of wastewater. Vessels can be filled with the carbon and the water then can be passed through these fixed beds assuring good contact between the water and solid. As the water passes through the beds, the organic content decreases and the carbon becomes loaded with the removed contaminants.

Eventually the carbon nearest the feed point becomes loaded to capacity and must be replaced by fresh or reactivated carbon. The replacement carbon would not actually be added near the water feed point, but would be added to the system where the treated water exits. This countercurrent method of contacting solid and liquid gives the most efficient utilization of carbon. It can be accomplished in a number of ways, the simplest being the use of multiple contractors or columns in series. In this arrangement, the first contactor of carbon is replaced when exhausted and the flow of water is changed to make that contactor last in the series.

To make the cost of operation reasonable, exhausted carbon must be reactivated and reused. Thermal reactivation is presently the only practical method. Using a multiple-hearth furnace or rotary kiln, the exhausted carbon is heated to about 1700°F in a steam-air atmosphere. This procedure burns off the adsorbed organics and restores the carbon to nearly virgin condition.

Experimental Investigations

Pomona Pilot Treatment Plant - Extensive work (3,4,5,6,7,8) has shown the technical feasibility of using granular activated carbon to remove organic material from wastewater. As a result of these laboratory and small pilot-scale studies, a large pilot plant was constructed. The site is the Pomona Research Facility. The pilot plant includes a 200-gpm carbon treatment plant and reactivating furnace.

The treatment plant (9) uses four carbon columns in series with the water flowing downward in each column. Details of column construction are shown in Figure 10. Each column is 6 ft in diameter and about 16 ft high. Construction is of steel with a tar-epoxy lining. The perforated screen on which the carbon is supported is of stainless steel. Maximum pressure is 50 psig. Provision is made for backwash and surface wash. Each column holds 6650 lb of water-treating carbon.* That amount of carbon fills the column to a depth of 9.5 ft. Characteristics of the carbon are shown in Table 7.

A 30-in. diameter six-hearth furnace** is used to reactivate the spent carbon. The furnace is equipped with gas burners and points of injection for steam and excess air. Maximum temperature is about 1700°F. The contacting system and the furnace are shown in Figure 11.

Chlorinated secondary effluent with no further pretreatment is fed to the system of carbon contactors. The elimination of a sand filtration step was not attempted in earlier carbon work. The low suspended solids content of the

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*Pittsburgh Activated Carbon Co., Pittsburgh, Pa.

**Bartlet-Snow-Pacific Inc., Cleveland, Ohio

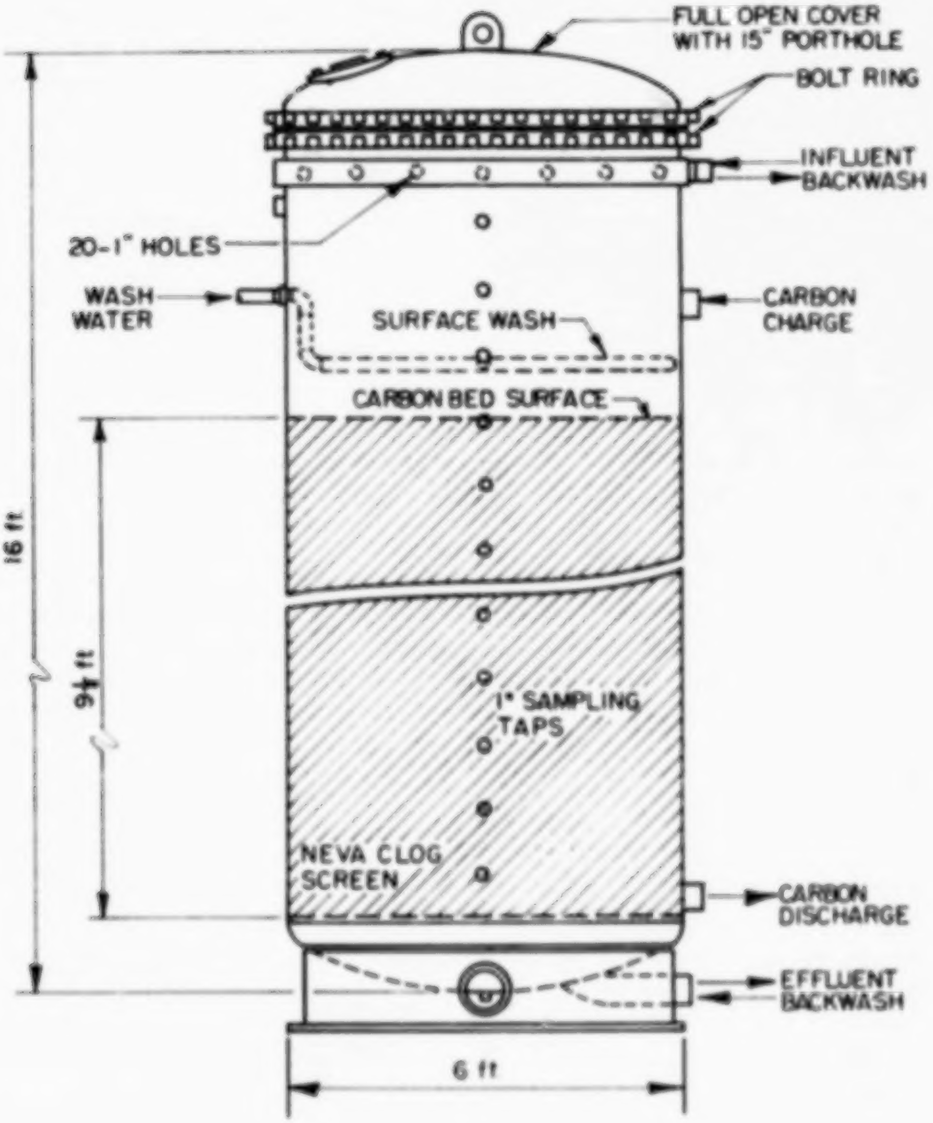
FULL OPEN COVER
WITH 15" PORTHOLE
BOLT RING
INFLUENT
BACKWASH
20-1" HOLES
WASH
WATER
SURFACE WASH
CARBON
CHARGE
CARBON BED SURFACE
16 ft
9 ft
1" SAMPLING
TAPS
NEVA CLOG
SCREEN
CARBON
DISCHARGE
EFFLUENT
BACKWASH
6 ft

Figure 10. Pilot carbon contactor.

Pomona effluent, however, makes filtration unnecessary. Because there is no provision for suspended solids removal from the feed stream, there is sufficient buildup of solids on the first contactor to make daily backwash necessary. Backwash is carried out with secondary effluent at a maximum rate of 200 gpm using a total flow of about 5000 gal. Operation of the system is continued until there is a significant breakthrough of soluble organics in the product water. The concept of breakthrough is somewhat nebulous here because there is at all times

Table 7. CARBON CHARACTERISTICS

Iodine Number	1100
Methylene Blue Number	300
Molasses Number	220
Apparent Density	0.47 g/ml
Ash Content	5%
Mean Particle	0.85 mm
Mesh Size	16 x 40

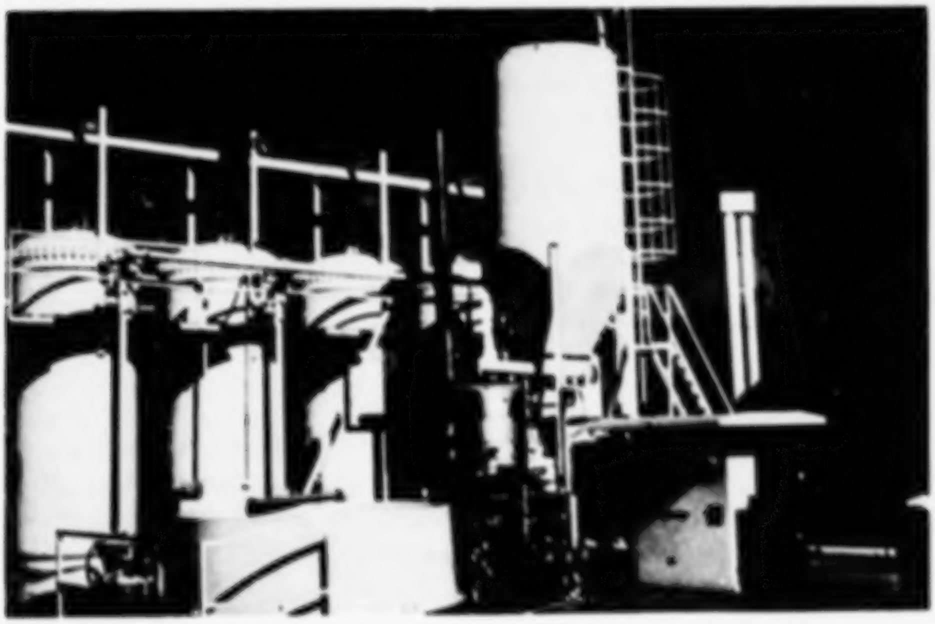

Figure 11. 200 gpm granular activated carbon pilot plant at Pomona, California. The carbon contractors are on the left. In the center is the six-hearth furnace for reactivating the carbon when it is exhausted. The raised tank to the right of the furnace holds drained carbon to be reactivated. The low tank to the left is used to quench the carbon in water when it leaves the furnace. Carbon is transported hydraulically to and from the carbon columns.

a small organic content in the product water that slowly increases with time. It has been found, however, that approximately 20,000,000 gal. of water can be treated before the product-water COD reaches a level of 12 mg/1. The average organic content will be somewhat less than 12 mg/1. When 20,000,000 gal. of water have been treated, operation is stopped and the carbon in the first contactor is reactivated. This is done by hydraulically conveying the carbon to a dewatering tank, reactivating in the multiple-hearth furnace, quenching, and conveying hydraulically back into the contactor. The flow pattern through the system is then changed so that the former second column becomes the first in line and the reactivated column becomes the fourth in line.

Performance of the carbon adsorption system during more than a year of operation is shown in Table 8. During this time, the carbon in all but the last column was reactivated once. Regeneration losses averaged about 10 percent. More than 90 percent suspended solids removal and 80 percent COD removal was achieved. Good removal of color and odor was also achieved. Dissolved COD removal, which is a better measure of removal by adsorption than total COD, was 77 percent. A soluble-COD loading on the carbon of 60 lb/100 lb carbon was obtained. Methylene blue detectable detergent removal was excellent, the concentration in the product being 0.1 mg/l or less. Results from continued operation of the system have not shown a significant decline in performance.

Although Table 8 indicates a sizable reduction in nitrate concentration, this is not a result of adsorption. It is due to biological action within the carbon column. Biological activity undoubtedly also aids organic removal. If a carbon column is operated well beyond the point of exhaustion of adsorption capacity, it will continue to remove some organics because of biological degradation.

Table 8. AVERAGE WATER QUALITY CHARACTERISTICS OF THE CARBON COLUMN AT THE POMONA RESEARCH FACILITY

June 1965 to August 1966

Parameter		Column Influent	Column Effluent
Suspended Solids	mg/l	10	<1
C O D	mg/l	47	9.5
Dissolved C O D	mg/l	31	7
T O C	mg/l	13	2.5
Nitrate, as N	mg/l	6.7	3.7
Turbidity	J T U	10.3	1.6
Color		30	3
Odor		12	1
Carbon Chloroform Extract	mg/l	-	0.014

Experience obtained from operation of the 200-gpm Pomona pilot plant was used in making a cost estimate for a 10-mgd plant. Using a four-stage system similar to the pilot plant and assuming a 10-percent loss of carbon during regeneration, the total treatment cost is estimated to be 8.3¢/1,000 gal.

Other Pomona Pilot Studies - Using a single contactor of the design used in the 200-gpm pilot plant, a study was begun to determine the effect of multiple reactivation. With one column, reactivation of the same batch of carbon can be carried out at 4 times the frequency of the 4-contactor system. The carbon in the column, which originally had the characteristics given in Table 7, is reactivated after treating about 20 million gal. water. After three reactivations, the iodine number, a measure of adsorbent surface, had declined from 1100 to less than 800. Additional reactivations have shown a further decline in iodine number to about 700. A parallel decline in adsorption capacity for soluble organics has been observed. This is shown in Figure 12 for seven reactivations. Data for additional reactivations are required to determine where the curve will finally level out. Although the carbon loadings in Figure 12 are for 9 ft of carbon and cannot be compared exactly with the loadings for the 36 ft of carbon in the

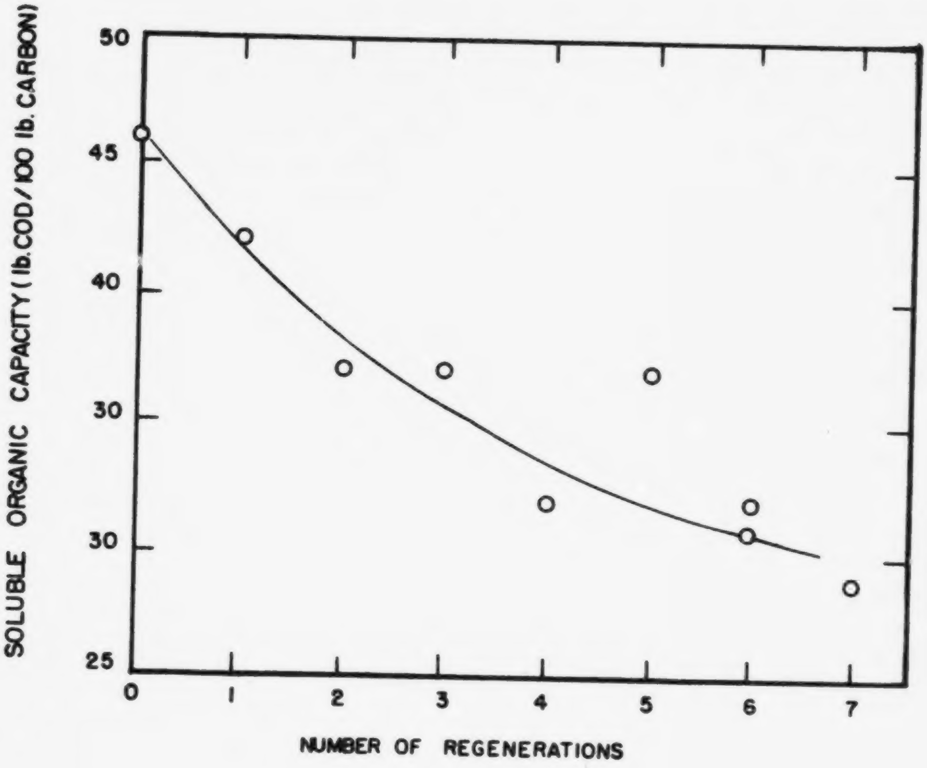

Figure 12. Effect of reactivation on absorption capacity.

200-gpm carbon pilot plant, it can be expected that some decline in performance of the pilot plant will occur. To maintain the product quality that was obtained for the first year of operation will require more frequent reactivation. Carbon losses experienced during the multiple-reactivation study have been about 10 percent, the same as for the 200-gpm pilot plant. The relatively small size of the reactivating equipment and short, intermittent furnace runs prevent the losses from being reduced to levels found in other carbon applications. It is believed that losses in a larger plant can be reduced to 5 percent or less.

For operation of the large columns, a hydraulic application rate of 7 gpm/ft ^{2} was chosen. This choice was based more upon pressure-drop considerations than mass-transfer considerations since it was not known exactly what the effect of velocity on mass-transfer rate might be. The first of several studies to determine this effect has been completed. Two-inch diameter columns were operated in parallel at different rates using diatomaceous-earth-filtered secondary effluent. Three rates chosen were 4, 7, and 10 gpm/ft ^{2} TOC was used as a measure of column performance. Data for 4 and 10 gpm/ft ^{2} as a function of empty column residence time are shown in Figure 13. To a good approximation, the removal obtained depends only on the contact time between carbon and water over the velocity range investigated. This is a very important point in design of adsorbers since, from a mass-transfer standpoint, only total system volume need be considered, not column geometry. It must be emphasized, however, that the data of Figure 13 were obtained on fresh carbon. Velocity may affect the mass transfer rate when carbon has been in contact with wastewater for long periods of time. Further study is required.

Laboratory Studies - A study was made (10) to determine the effect of feed turbidity upon the quality of the product from a carbon column. Batches of secondary effluent were collected and divided into two parts. One part was filtered through a dual media filter to remove large particles, but retain the fine suspended material contributing to turbidity; the other part was chemically clarified using alum or lime for removal of nearly all turbidity. The filtered water was then passed through a carbon column at 2 gpm/ft.^{2} Length of the column was 163 cm for most runs. Some work was done with a 305-cm column. The filtered water was followed by the chemically clarified water. Results of these runs are shown in Table 9. Effluents labeled A were from a trickling filter; those labeled B and C were from activated sludge plants. It is obvious that the total organic carbon in the product water is due largely to the turbidity that remains. Appreciable turbidity removal occurred in the column. Average turbidity removals of 31 percent, and 44 percent were found in the 163-cm and 305-cm column respectively. The logarithm of the fraction remaining turbidity was pro-

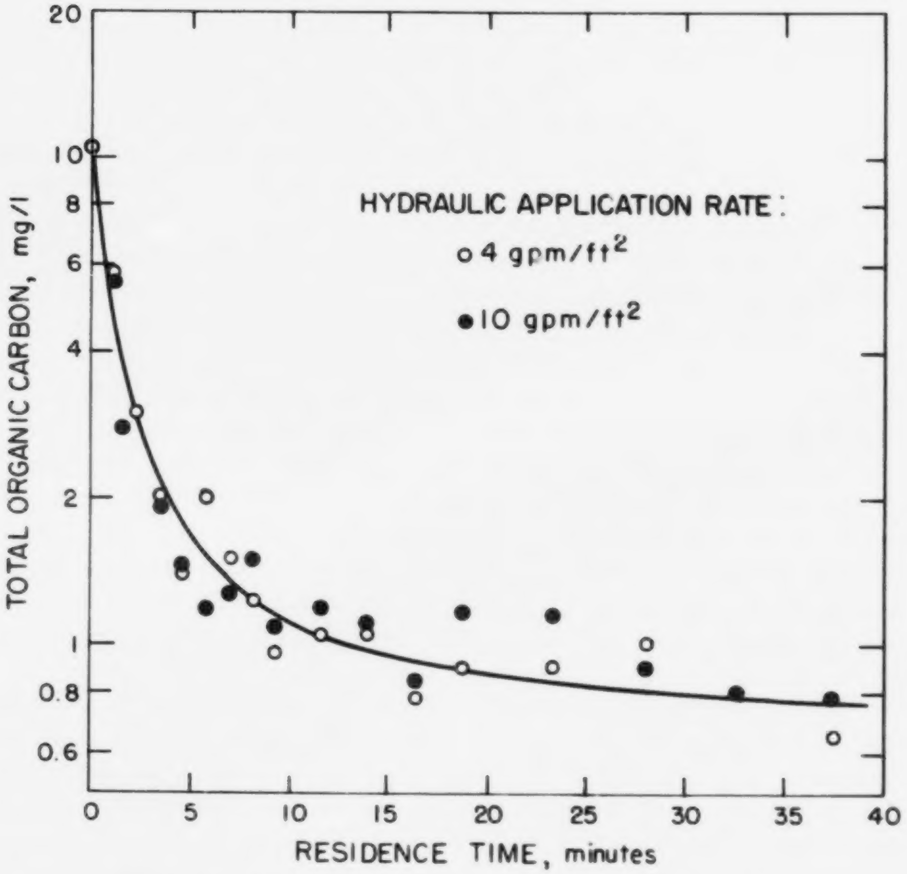

Figure 13. Effect of feed rate on carbon column performance.

Table 9. EFFECT OF FEED TURBIDITY ON CARBON COLUMN PRODUCT QUALITY

Pretreatment: Filtered

	Turb. Units		TOC (mg/l)	
Effluents	In	Out	In	Out
A-1[a]	--	--	--	--
A-2[b]	--	--	--	--
A-4	10	6.7	17	4
A-5	15	10	19	5
B-3	7.1	5.5	14	4
B-4	15	8.7	18	5
C-2	8.8	6.5	12	2

Chemically Clarified and Filtered

	Dose	Turb. Units		TOC (mg/l)	
Chem.	(mg/l)	In	Out	In	Out
Al	260	19	11	33	4
Al	400	1.1	0.6	30	1
Al	300	0.2	0.1	9	0
Ca	303	0.5	0.3	11	0
Al	350	0.2	0.2	8	0
Ca	227	1.6	1.3	13	0
Ca	151	0.9	0.7	9	0

[a] Partially clarified with alum.

[b] 38-minute empty bed contact time; all others 20-minute bed contact time.

portional to the column length, or residence time, over the range of carbon column lengths studied.

Carbon column treatment of chemically clarified secondary effluent was further studied on a continuous basis. The secondary effluent was batch-clarified with 300 mg/l lime, chlorinated, and fed at a steady rate of 1.85 gpm/ft ^{2} to a 10 ft column of 16 x 40 mesh carbon. The column was constructed of 1-ft sections, each of which could be removed separately. The product was monitored for turbidity, ammonia, TOC, and ultraviolet absorbance at 2537 Å. The ultraviolet absorbance has been found to correlate with TOC and could provide a useful control method for carbon column operation. After operating for 103 days, there was significant organic breakthrough. Two 1-ft sections were removed from the top of the column and two new sections were added at the bottom. Breakthrough then occurred more frequently and carbon changes were required every 31 days. Clarification and chlorination did not prevent biological growths from occurring in the upper part of the column. These growths increased column pressure-drop noticeably. Backwashing with 90°C water for one hour did not prevent the growths, but did slightly extend carbon life. Both hot and cold water backwash effectively controlled pressure-drop increase.

Table 9 shows that very little organic material escapes from a column containing unspent carbon when the feed is well-treated clarified secondary effluent. If secondary treatment is poor, however, there usually is breakthrough of soluble organics even when the carbon is new. This result should be expected since certain groups of materials in poorly treated wastewater are known to resist adsorption on carbon. To demonstrate the poor adsorbability of some examples from some of these groups, batch-adsorption tests were run using 1000 mg/l of carbon and solutions of pure materials. Although the experiments were done with powdered carbon, the results apply equally well to granular carbon. Concentrations of compounds tested were 100 mg/l. Table 10 shows the results based on TOC measurements. Amino acids and sodium salts of fatty acids with

Table 10. CARBON ADSORPTION OF PURE MATERIALS KNOWN TO BE POORLY ADSORBED

Substance	% Adsorbed	Substance	% Adsorbed
Glucose	8	Sodium Formate (pH 7.5)	2
Sucrose	37	Sodium Acetate "	1
Glycine	1	Sodium Propionate "	4
Alanine	1	Sodium Butyrate "	4
Serine	0	Sodium Valerate "	8
N Phenyl glycine	48	Sodium Caprylate "	54

less than 8 carbon atoms were only slightly adsorbed. Glucose is also only slightly adsorbed. Sucrose, surprisingly, is appreciably adsorbed, but probably would be displaced easily by more adsorbable materials.

Adsorption tests on pure materials provide data to explain carbon-column breakthrough, but do not conclusively prove what materials are breaking through. To determine this requires expensive and time-consuming analysis of a very dilute multicomponent solution. Some work along these lines has been carried out. Analysis of several carbon-column effluent samples failed to show significant amounts of non-carbohydrate carbonyl compounds, total carbohydrates and reducing sugars. One sample from an overloaded carbon column showed 1.8 mg/l or 13 percent of the residual TOC as carbohydrate. Analysis of another carbon-column effluent sample showed removal of straight-chain acids from propionic through caproic. About 90 percent of the acetic acid, but less than 50 percent of the formic acid was removed.

Future Work

The technical and economic feasibility of granular activated carbon treatment of secondary effluent has been established. Further studies will be concerned primarily with improving the treatment method. Work at Pomona will be continued on the large pilot columns to obtain more firm figures on carbon requirements. A small pilot-scale study using downflow columns will be made to compare the effectiveness of four or five different granular carbons. The effect of particle size and carbon source will be investigated. Further studies of velocity effects will be conducted. A contract study is planned of parameters affecting reactivation. Plans have also been made to appraise well known carbon-contactor types including that at Pomona. Included will be an experimental investigation of a fluidized bed contactor. Further investigation of hot water backwash will be made. Experience has shown that backwash is required for pressure-drop control and the use of hot water will give some degree of reactivation.

Some work may be undertaken on treatment of primary effluent. Earlier work did not appear promising (7), but the desirability of finding an economical replacement for secondary treatment or a process that does the equivalent of secondary and tertiary treatment justifies further investigation.

ADSORPTION ON POWDERED ACTIVATED CARBON

Principle of Operation

Powdered activated carbon adsorbs soluble organics from wastewater just as granular carbon does. Because of the much smaller average particle size, about 10 microns, the adsorption rate is much more rapid. The small particle size results in high pressure drops for fixed-bed operation. Some other form of contacting must, therefore, be used. A combination of mixing, flocculation, settling, and filtration if necessary is one possible system. This system has the advantage of clarifying the water at the same time that adsorption is taking place. One mixer-flocculator-settler combination does not, however, allow advantage to be taken of countercurrent contacting and the resulting lower carbon requirements. For countercurrent action, two or more mixer-flocculator-settler combinations must be used in series, with the fresh carbon being added to the last mixer. This carbon, upon settling in the last settler, is then added to the second last mixer. The movement of carbon upstream is continued until the first mixer is reached.

Reactivation of the exhausted carbon is needed to obtain reasonable operating costs. No suitable procedures for reactivation of powdered carbon are yet available. Thermal methods will probably be the only ones feasible.

Experimental Investigations

Dorr-Oliver Inc. conducted the initial laboratory scale study (11) of powdered-carbon treatment of wastewater. They compared contacting methods and demonstrated the practicability of the mixer-flocculator-settler method using a polyelectrolyte to improve flocculation. They also showed the saving

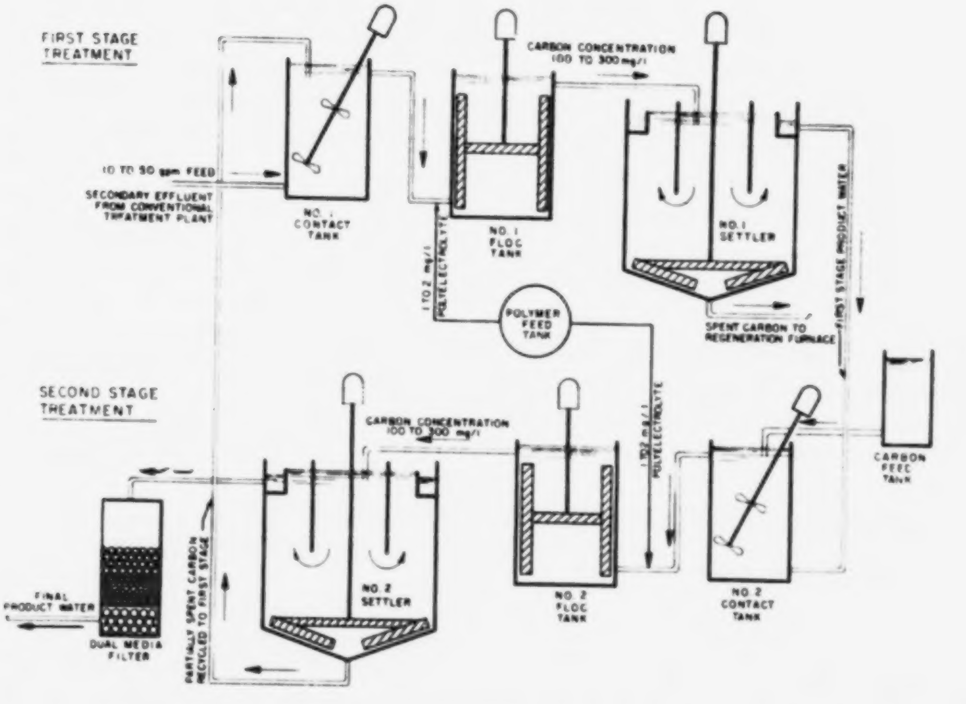
FIRST STAGE TREATMENT
CARBON CONCENTRATION 100 TO 300 mg/l
10 TO 50 gpm FEED
SECONDARY EFFLUENT FROM CONVENTIONAL TREATMENT PLANT
NO. 1 CONTACT TANK
NO. 1 FLOC TANK
NO. 1 SETTLER
1 TO 2 mg/l POLYELECTROLYTE
POLYMER FEED TANK
SPENT CARBON TO REGENERATION FURNACE
FIRST STAGE PRODUCT WATER
SECOND STAGE TREATMENT
CARBON CONCENTRATION 100 TO 300 mg/l
1 TO 2 mg/l POLYELECTROLYTE
CARBON FEED TANK
FINAL PRODUCT WATER
DUAL MEDIA FILTER
PARTIALLY SPENT CARBON RECYCLED TO FIRST STAGE
NO. 2 SETTLER
NO. 2 FLOC TANK
NO. 2 CONTACT TANK

Figure 14. Powdered carbon adsorption pilot plant, Lebanon, Ohio.

that results from using two-stage countercurrent contacting. A preliminary study of thermal reactivation of the carbon suggested that a steam atmosphere and temperatures as low as 750°F might be used. Costs for the process were estimated at less than 10¢/1,000 gal.

As a result of the laboratory work, a 10-gpm pilot system was designed and constructed at the Lebanon, Ohio Pilot Plant. The two-stage countercurrent system is shown in Figures 14 and 15. Each stage consists of a 100-gal. contact tank, a 200-gal. flocculation tank, and a 600-gal. settler. Following the second

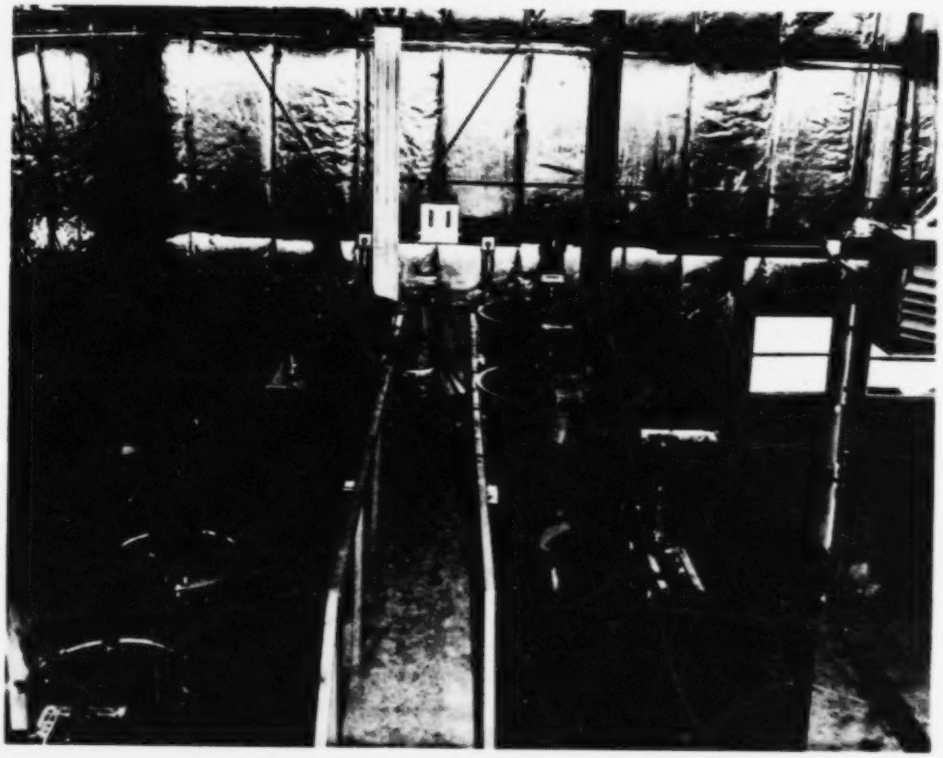

Figure 15. Powdered carbon pilot plant at Lebanon, Ohio. The row of tanks on each side of the walk makes up one stage of the two-stage contacting system. Wastewater enters the small tank on the right in the rear. Here it is mixed with carbon already used in the stage to the left of the walk. In the second tank on the right, the carbon-water mixture is slowly stirred in the presence of a small amount of polyelectrolyte to cause flocculation. In the third tank the solids are settled from the water. These solids are largely spent carbon. The water then passes to the second stage where it is treated with fresh carbon. Following the second settler is a dual-media filter for removal of small amounts of carbon that do not settle out. Studies to develop methods for reactivating the waste carbon for reuse are being planned.

Table 11. POWDERED CARBON TREATMENT OF SECONDARY EFFLUENT

Feed Rate (gpm)	Carbon Concentration (mg/l)	Product TOC (mg/l)
10	100	2.0, 1.7
	200	0.9, 1.0, 1.7, 1.4
15	200	1.7, 1.4
	250	1.7
20	100	1.5
	200	2.3

Feed TOC varied from 11 to 36 mg/l.

stage is a dual-media filter for removal of small amounts of carbon escaping the second settler. Aqua Nuchar A,* usually in concentrations of 100 or 200 mg/1, was the carbon used in the pilot plant. The polyelectrolyte used to improve flocculation has been Primafloc C-7. Concentration of polyelectrolyte is 0.5 mg/1 in the first stage and 1.0 mg/1 in the second stage.

Some early results from the pilot plant are shown in Table 11. Results are the average over at least two days of operation. Although tank sizes were designed for a 10-gpm rate, the data show that higher rates do not seriously affect product quality. Higher carbon concentrations do not in all cases give better product quality. At 20 gpm, for example, 200 mg/1 of carbon gave a poorer product than 100 mg/1. The TOC of the feed was higher for the 100 mg/1 run, therefore, the feed concentration is not responsible for the inconsistency. The nature of the organics appears to be the most important factor. More recent data indicate that generally better results are obtained with higher carbon concentrations, as one would expect. Turbidities of the product water are usually less than 1 JTU.

Figure 16 shows what contaminant loadings on the carbon may be obtained. Included in the loading values are suspended solids which are actually removed by flocculation. The line through the 100-mg/1 data has been drawn at twice the loadings of the line through the 200-mg/1 data. The fact that the 100 mg/1 data lie very near the line indicates that the total organic removal capability of the process is not greatly affected by carbon concentration in the concentration range investigated. On the average, however, the higher carbon

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**West Virginia Pulp & Paper Co., Covington, Va.*

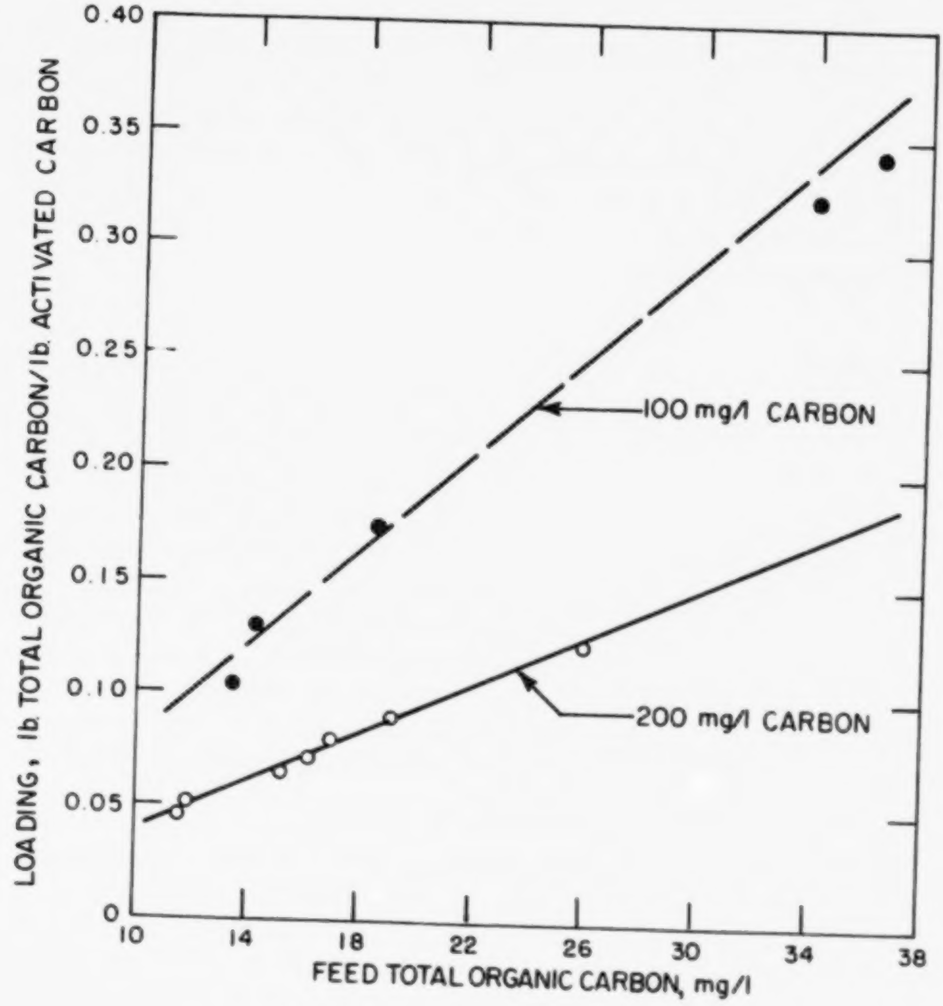


Figure 16. Powdered carbon loadings.

concentration gives slightly lower TOC values in the product. To obtain very high-quality water, at least 200 mg/1 would be required.

The economics of powdered carbon treatment cannot be accurately predicted until more is known about the feasibility of reactivation. If the carbon can be reactivated with not more than 15 percent loss, the total operating cost, including amortization of equipment, should be about 12¢/1,000 gal. for a 10-mgd plant.

Future Work

The feasibility of reactivation of powdered carbon is the most important question remaining to be answered. Present plans are to investigate several possible methods on a small scale. For any methods showing promise, pilot units will be constructed and used to reactivate the carbon from the 10-gpm pilot plant.

Additional studies to be carried out will include evaluation of other carbons and equipment configurations. Treatment of primary effluent will also be investigated. The suspended solids removal that occurs along with soluble organic removal may make possible the production of better-than-secondary-effluent quality water directly from primary effluent.

OXIDATION

Principle of Operation

Although the conventional biological processes used to treat wastewater are oxidation processes, they do not completely oxidize the organic material present. Chemical oxidation has the potential for removing the remaining organics. These would be converted to carbon dioxide, water, oxides of nitrogen, and oxides of other elements. Another possible application is the polishing of carbon-treated water for destruction of remaining traces of organic materials. Oxidation methods that might be employed include use of active oxygen species such as ozone, hydrogen peroxide, and hydroxyl free radical; oxidation with molecular oxygen; catalytic oxidation with molecular oxygen; use of chlorine and derivitives; use of oxy-acids and their salts such as potassium permanganate; and electrochemical treatment.

The first method, use of active oxygen species, is particularly interesting because of the ways other than direct addition of ozone and hydrogen peroxide in which the active species may be introduced into the water. One method is by corona discharge in moist air in proximity to the water to be treated. Corona discharge is a high-voltage, high-frequency (10,000 cycles per second), and low-temperature electrical discharge. A number of free radicals and other active oxidizing species are formed in the gas phase and are transferred to the water where oxidation occurs. Another way to produce active oxygen species is by radiation from radioactive sources. In this case, the radiation causes free radical formation directly in the water by breaking up water molecules.

Experimental Investigations

Although early laboratory-scale (6,12) studies of a number of oxidation methods indicated those methods were not practical, several promising processes remained. One of these was corona discharge, a study of which was undertaken by the General Electric Company. Figure 17 shows a laboratory reactor that was used to obtain data. It was designed so that the water encircled the inside of the outer tube and fell in a thin film through the area of electrical discharge. Table 12 shows results for some synthetic and actual wastewater samples. Although

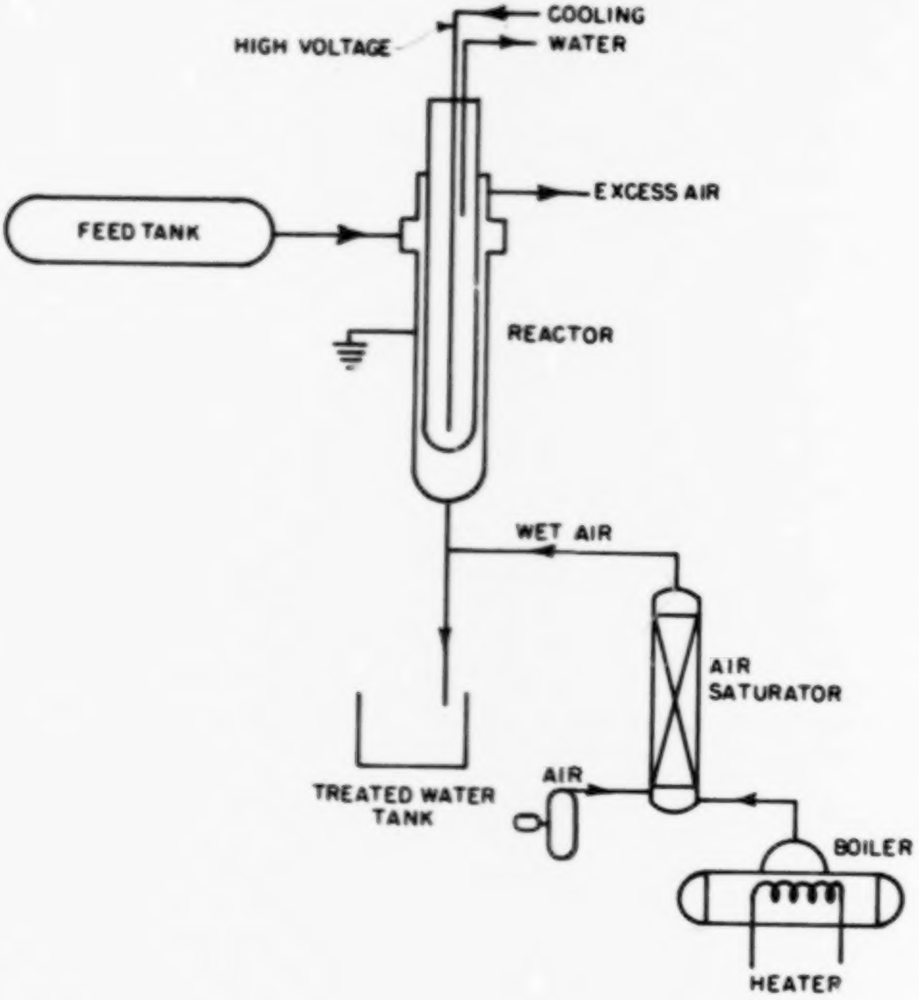

COOLING
WATER
HIGH VOLTAGE
EXCESS AIR
FEED TANK
REACTOR
WET AIR
AIR
SATURATOR
TREATED WATER
TANK
AIR
BOILER
HEATER

Figure 17. Equipment for studying corona discharge treatment of wastewater.

there is considerable scatter in the results, it is obvious that the power requirements are impractically high. Of interest is the fact that the oxidation of ferrous ion to ferric ion required about an order-of-magnitude less power. Unless much more efficient use can be made of the power for oxidizing organics, the process is not economically feasible.

A short investigation was made of oxidation by nuclear radiation. Using a cobalt-60 source for 48 hours at an approximate dose of 1.2×10^3 rads/hr, only 20 percent of the COD and 8 percent of the organic carbon was removed from a

Table 12. CORONA OXIDATION

Power Level: 80 watts — Liquid-feed rate: 0.36 liters/min

System	Initial COD	ΔCOD	meq/watt-hr	kwh/1,000 gal/10 COD
Benzoic Acid	20.4	2.2	0.075	63.7
Benzoic Acid	195.0	3.8	0.129	36.9
Benzoic Acid	33.5	1.1	0.037	127.0
ABS	22.1	3.0	0.100	46.7
ABS	21.7	3.5	0.119	40.1
Secondary Eff. I	75.6	0.2	0.014	700.0
Eff. I and H_2O	36.4	1.5	0.050	93.5
Secondary Eff. II	72.2	5.1	0.170	27.5
Eff. II and H_2O	36.1	--	--	--
Carbon Eff.	2.0	1.4	0.047	100.0
Average power: kwh/1,000 gal/10 COD				58.0

wastewater sample. The most optimistic cost estimate for oxidation of a normal waste effluent by radioactivity is 50¢/1,000 gal. if the source costs 10¢/curie. This does not include equipment costs.

Future Work

Plans have been made to study three more oxidation processes: ozone treatment, catalytic air oxidation, and light-catalyzed chlorine oxidation. Ozone is known to be effective in removing organic tastes and odors from surface waters. Catalytic oxidation is of interest because of its simplicity and possible low cost. Oxidation with chlorine could also be simply done and would have the added advantage of carrying out disinfection with a material that is readily accepted by the public.

FOAM SEPARATION

Until recently, accumulations of foam on our nation's waterways from discharge of sewage were becoming increasingly frequent and foam at sewage treatment plants was becoming a serious problem. The major cause of this foam was non-biodegradable detergents of the anionic type. A process was developed in which sewage was deliberately aerated to form foam and this was then removed. Because of the tendency of detergents to concentrate in the foam, the result was a relatively low-foaming product water. In addition to removal of detergents, it was also found that removal of other soluble organics and suspended material occurred. In laboratory studies, about 25 percent of the organics were removed from primary and secondary effluents (13, 14). Pilot plant operation at Pomona, California, showed as high as 40-percent removal from secondary effluent. Estimated cost of the process was less than 2¢/1,000 gal. for plants of 10-mgd capacity.

In 1965, more highly degradable or "soft" detergents began to replace the older "hard" types. The result was lower detergent concentrations in treated sewage effluents and streams. The need for and interest in a defoaming process decreased. As a result, study of the foam separation process ended. With increased awareness of the public in the problem of water pollution, it is doubtful whether highly-foaming non-biodegradable materials with as widespread a use as detergents will be marketed in the future. If foaming does again become a problem, however, a proven process will be available for control.

INORGANIC REMOVAL

Secondary effluent usually contains 300 to 400 mg/l more minerals than are found in the water supply to a municipality. The materials making up this increment are, except for ammonia, nitrate, and phosphate, commonly found in surface waters. A list of the predominant ones and approximate average values for their concentrations in once-used water, as well as concentration increases, are shown in Table 13. In the usually observed concentrations they are nearly all harmless, although not necessarily without taste. In the case of multiple reuse, however, the concentrations will all build up rapidly to prohibitive levels. The rate of build-up can easily be demonstrated by adding to the secondary effluent

Table 13. AVERAGE MINERAL COMPOSITION OF SECONDARY EFFLUENT AND CONCENTRATION INCREASES DURING USE (15)

Material	Concentration in Secondary Effluent (mg/l)	Increase During Use (mg/l)
Sodium	124	66
Potassium	12	10
Ammonium*	-	Essentially the concentration in secondary effluent
Calcium	66	18
Magnesium	19	6
Chloride	143	74
Nitrate*	-	Slightly less than the concentration in secondary effluent
Bicarbonate	296	100
Sulfate	84	28
Silicate	43	15
Phosphate	25	24
Total Dissolved Solids	703	320

*In most secondary effluents the predominant form of inorganic nitrogen is ammonium ion with only traces of the oxygen-containing forms, nitrite and nitrate ion. If nitrification is carried out at the treatment plant, however, nitrate will be the predominant form with only traces of ammonium and nitrite ion. It is difficult, therefore, to give an average value for the separate nitrogen forms. A very rough average value for total inorganic nitrogen is 20 mg/l. The average tap water contains about 1 mg/l of inorganic nitrogen and this is almost all present as nitrate ion. Nearly all the inorganic nitrogen found in secondary effluent must be considered, therefore, to have been added during use.

concentrations, an incremental increase for each additional reuse. For the purpose of preventing mineral build-up, methods to demineralize wastewater are being studied.

From a cost standpoint it is important to know what fraction of minerals must be removed. Although this fraction will obviously be related to the amount of minerals added, in an actual situation it will also depend upon the amount of unused dilution water available, the selectivity of the removal process for the various ions, and the maximum allowable concentrations. A study (15) of complete recycle for 22 municipalities, assuming no consumptive losses or dilution-water additions and using the non-selective distillation process for demineralization, indicated that between 24 and 64 percent of the wastewater would have to be distilled depending on the municipality chosen. Because distillation is assumed to remove all inorganics, except ammonia, these percentages also represent fraction removal. A rough average figure for necessary inorganic removal is 40 percent.

Ammonia would not be tolerable in most waters at a concentration of 1 mg/l or more. Fractional removal would not be adequate. Essentially all the ammonia must be removed either by nitrification in the biological treatment process or by an auxiliary process.

All practical demineralization processes studied thus far have the undesirable property of producing a volume of concentrated waste that is likely to be between 5 and 10 percent of the product. The volume of concentrate cannot be further reduced without the use of specially designed auxiliary equipment because low-solubility materials begin to precipitate out as scale on heat or mass-transfer surfaces. The result is a sizable volume of liquid that must be disposed of in such a way as to prevent further pollution. Depending upon location, the cost of waste disposal can vary widely, but in no case should it be considered negligible.

DISTILLATION

Distillation is well known as a process for producing pure water when the feed contains only materials of low volatility. Recovery of potable water from properly pretreated seawater is a much-publicized large-scale application.

Principle of Operation

To carry out distillation at a reasonable cost, it is necessary to devise special equipment that will allow for multiple reuse of the heat needed to vaporize the water. Three general equipment types are employed: multiple effect evaporators, multistage flash evaporators, and vapor compression evaporators (6). The first two usually are operated with a feed temperature of about 212°F or higher; the third is often operated with a feed temperature less than 212°F. Operation at less than 212°F naturally requires vacuum conditions. Using these special types of distillation equipment, it now appears possible to distill seawater in multimillion-gpd installations for less than $1.00 per 1,000 gal. The cost is still somewhat higher than estimated for most of the advanced waste treatment processes. It should be possible to treat only part of the water by distillation for organic and mineral removal, however, and to treat the remaining fraction by a lower-cost organic-removal process (6). At the present cost of distillation the cost of product water from the split-treatment system would still be too high to consider for pollution control alone. Reuse for a high-quality water purpose would probably be the only justification for such a system.

Experimental Investigations

An initial desk-top study (16) suggested that multiple effect or multistage flash equipment, operating with feed temperatures as high as 350°F, should be most economical for wastewater application. A pilot-scale investigation (6) of the multistage flash evaporator operating on secondary effluent at temperatures above 260°F indicated several serious problems. Rapid organic fouling of heat-transfer surfaces occurred. The product water had a strong disagreeable odor even though the feed was almost odorless. Laboratory batch distillation of secondary effluents (17) at temperatures of 160, 212, and 340°F also gave products with objectionable odors. The odor was less at the lower temperatures and could be removed by aeration or carbon treatment. This work suggests that as low a distillation temperature as possible should be used to minimize organic contamination of the product-water.

In the laboratory investigation, ammonia carryover from all ammonia-containing samples proved to be a serious problem. Decomposition of organic nitrogen compounds increased the amount of available ammonia, especially at the highest temperature. Carryover could only be prevented by lowering the feed pH to about 3. Corrosion of common still-construction materials would be appreciable under these acid conditions.

Future Work

As a result of wastewater distillation work, it appears that distilling temperatures of 212°F or lower might be more practical than the very high temperature originally envisioned. Organic contamination of the product should be lower. Although there is no experimental proof, fouling would be expected to decrease at lower temperature. Tendency for scale formation would also decrease. Vapor compression, therefore, suggests itself as an appropriate type of distillation for future work. Unless the feed is a nitrified effluent, ammonia removal from the product will be necessary. Carbon treatment or aeration will be required for removal of odor-causing trace organics.

ELECTRODIALYSIS

Electrodialysis is being used to produce potable water by partially demineralizing brackish ground water in many water-short areas of the world. A plant at Buckeye, Arizona, has a capacity of 650,000 gpd. A plant being operated by the Office of Saline Water at Webster, South Dakota, has a capacity of 250,000 gpd. It is reasonable to assume that, technically, electrodialysis should be applicable to partial demineralization of wastewater. Because wastewater has a lower mineral content than brackish water, cost of the operation should, in fact, be less than for brackish water. Wastewater, however, contains organic contaminants not found in ground water and this factor will affect the economics of operation. It is therefore necessary to study the process in terms of the degree of pretreatment needed for practical operation. Because of the extensive pretreatment required, the product-water should be very high quality, suitable for many uses.

Principle of Operation

An electric potential impressed across a cell containing mineralized water will cause positively charged ions or cations to migrate to the negative electrode and negatively charged ions or anions to migrate to the positive electrode. If

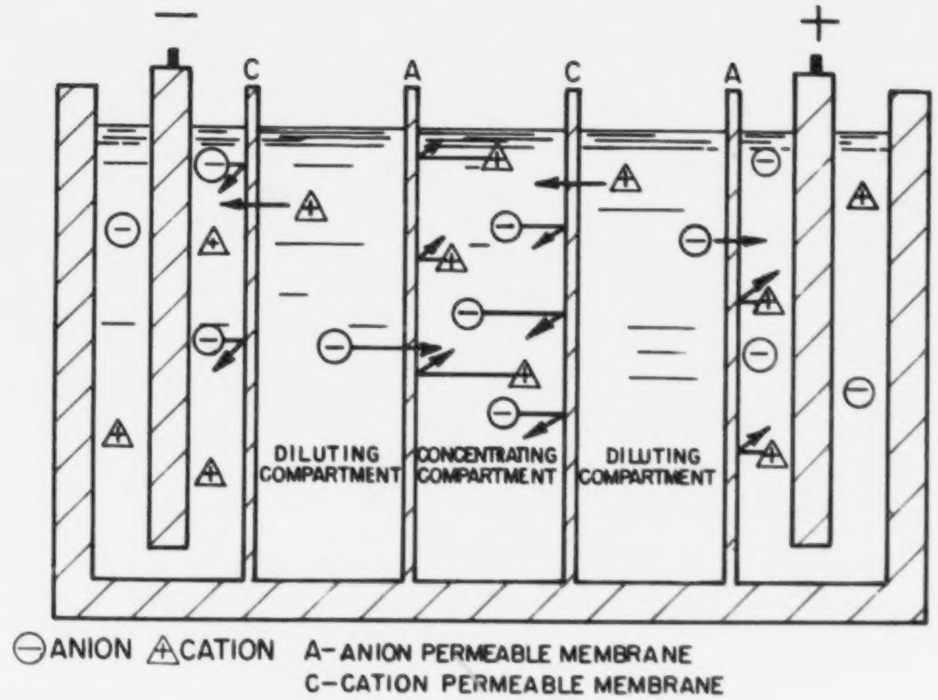

—
+
C
A
C
A
DILUTING COMPARTMENT
CONCENTRATING COMPARTMENT
DILUTING COMPARTMENT
⊖ANION
⊕CATION
A–ANION PERMEABLE MEMBRANE
C–CATION PERMEABLE MEMBRANE

Figure 18. Electrodialysis principle.

cation and anion-permeable membranes are placed alternately between the electrodes as shown in Figure 18, alternate compartments become more concentrated, while the intervening compartments become diluted. This separation process is called electrodialysis. Membranes that have the property of being permeable to only cations or anions are composed respectively of cation or anion exchange material similar to ion exchange beads. Many membranes can be placed between the electrodes forming many alternate dilute and concentrate compartments. Manifolds can then be added so that the membrane stack can be fed continuously and product and waste concentrate streams can be removed continuously.

The amount of electric current required to carry out demineralization is proportional to the number of ions removed from the diluting compartments. If the number of ions that must be removed becomes very large the electrical power consumption becomes uneconomical. To demineralize wastewater sufficiently to remove the mineral increment added during use requires only a small amount of electrical power.

Although the electrodialysis membranes freely pass common inorganic ions of either positive or negative charge, they do not necessarily permit passage

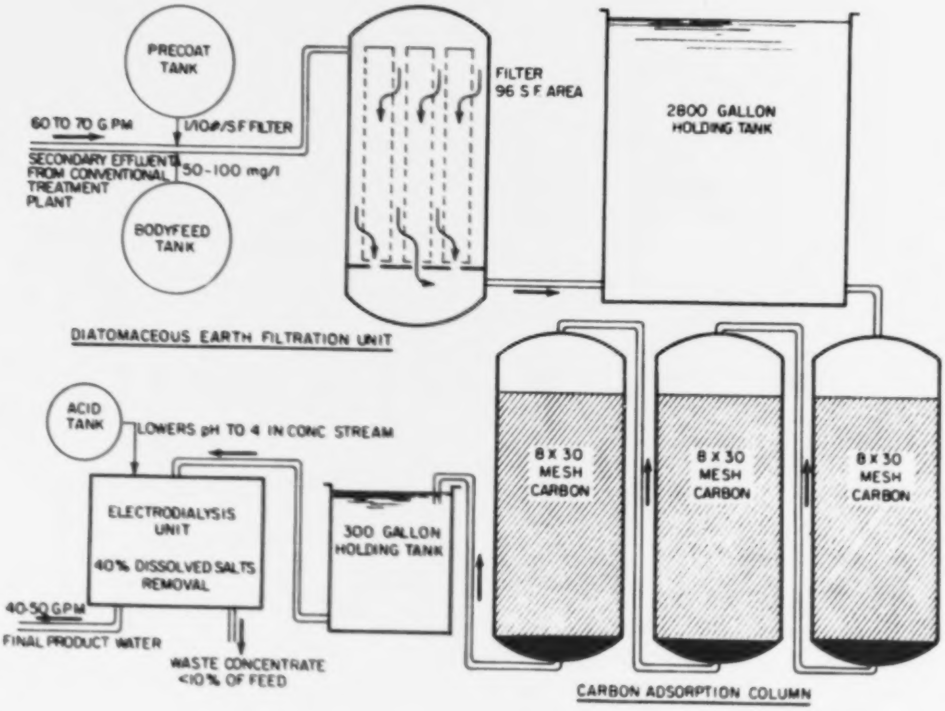

PRECOAT TANK
60 TO 70 G PM
1/10#/S F FILTER
SECONDARY EFFLUENT FROM CONVENTIONAL TREATMENT PLANT
50-100 mg/l
BODYFEED TANK
FILTER 96 S F AREA
2800 GALLON HOLDING TANK
DIATOMACEOUS EARTH FILTRATION UNIT
ACID TANK
LOWERS pH TO 4 IN CONC STREAM
ELECTRODIALYSIS UNIT
40% DISSOLVED SALTS REMOVAL
40-50 GPM
FINAL PRODUCT WATER
WASTE CONCENTRATE <10% OF FEED
300 GALLON HOLDING TANK
8 X 30 MESH CARBON
8 X 30 MESH CARBON
8 X 30 MESH CARBON
CARBON ADSORPTION COLUMN

Figure 19. Electrodialysis pilot plant, Lebanon, Ohio.

of larger charged particles such as large organic ions and colloids. These materials are, however, attracted to the membranes, especially the anionic membranes, by electrical forces. The result is a fouling of the membranes. The most obvious effect is an increase in electrical resistance that at constant stack voltage decreases the current and, therefore, the demineralizing capacity of the equipment.

Experimental Investigations

Laboratory-scale work (6, 18) indicated that electrodialysis should be practical for partial demineralization of properly pretreated wastewater. The pretreatment considered necessary was clarification for removal of most colloidal and larger size particulate matter, and carbon adsorption treatment for removal of soluble organics. To determine more realistically the feasibility of

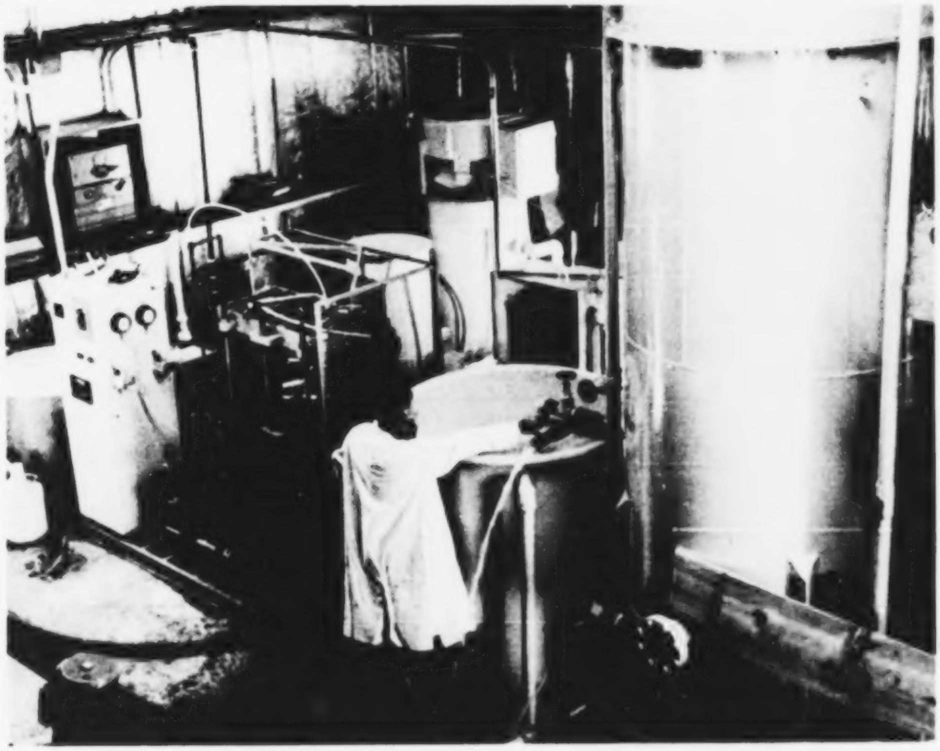
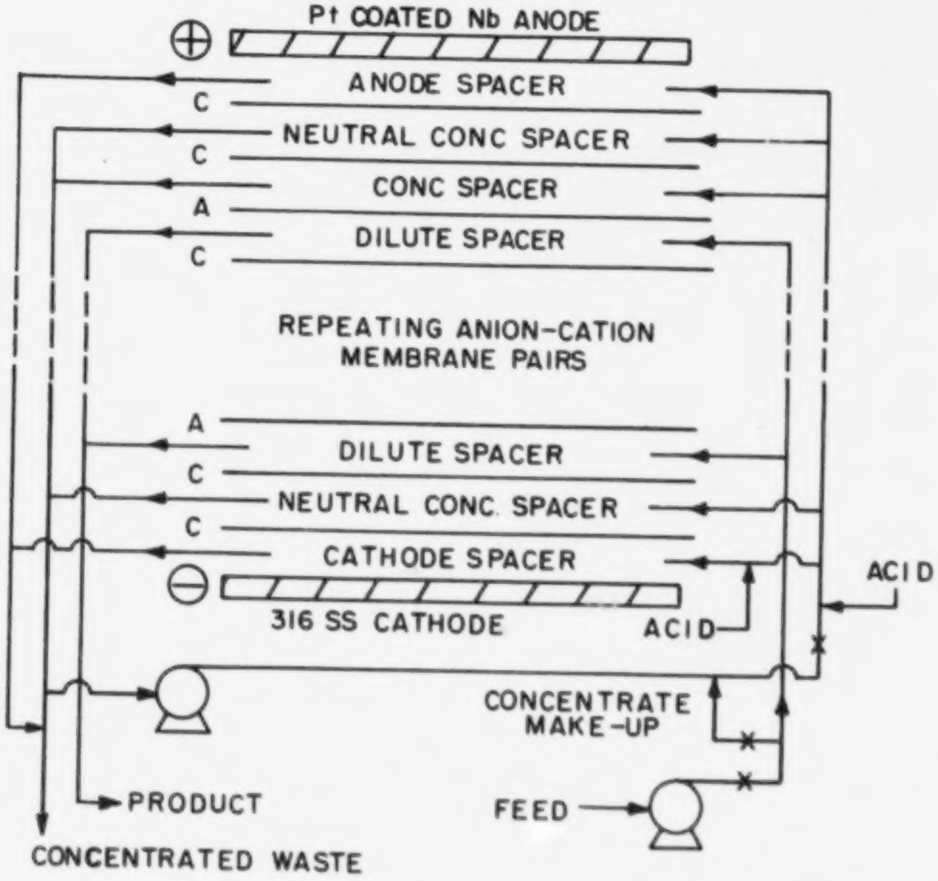


Figure 20. 50-gpm electrodialysis pilot plant at Lebanon, Ohio. The electrodialysis equipment is on the left. It is contained on a skid about four feet wide and six feet long. On the right is one of three carbon columns that operate in series to remove soluble organic materials from the electrodialysis feed. In the background are tanks associated with the diatomaceous earth filter used to clarify the wastewater before entering the carbon columns. The carbon columns are shown being started for an electrodialysis run.

electrodialysis, a pilot-scale system (19) was constructed and is being operated on secondary effluent from the Lebanon, Ohio Municipal Wastewater Treatment Plant. The advanced treatment system consists of a diatomaceous earth filter, carbon adsorption columns, and a 150-cell-pair Ionics Mark III* electrodialysis stack, designed for removal of about 40 percent of the total dissolved solids (TDS). The equipment is shown in Figures 19 and 20. The diatomaceous earth filter uses water-filtering-grade diatomaceous earth treated with alum. The columns contain 8 x 30 mesh granular activated carbon.** Figures 21 and 22 show the electrodialysis stack in more detail. Membranes are 18 x 40 in. and


Pt COATED Nb ANODE
ANODE SPACER
C
NEUTRAL CONC SPACER
C
CONC SPACER
A
DILUTE SPACER
C
REPEATING ANION-CATION MEMBRANE PAIRS
A
DILUTE SPACER
C
NEUTRAL CONC. SPACER
C
CATHODE SPACER
316 SS CATHODE
ACID
ACID
CONCENTRATE MAKE-UP
PRODUCT
FEED
CONCENTRATED WASTE

C – CATION MEMBRANE
A – ANION MEMBRANE

Figure 21. Electrodialysis stack details.

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*Ionics, Inc., Watertown, Mass.

**Pittsburgh Activated Carbon Co., Pittsburgh, Pa.

contain openings that form internal manifolds for the various liquid streams during operation. Spaces between membranes are of the tortuous path type. Acid feed to the concentrate stream is used to prevent calcium carbonate scale formation. Using 150 cell pairs, the product rate was 50 gpm and the amount of concentrated waste was 5 gpm. These rates were reduced to 42 gpm and 4 gpm respectively and the number of cell pairs was reduced to 125 to cut down the rate through the diatomaceous earth filter which was found to be underdesigned. Total running time has been more than 1,500 hrs.

During operation of the pilot plant only one serious problem has arisen, fouling of the anion membranes. Figure 23 shows the effect that fouling has on the demineralizing capability during operation. The top and bottom curves indicate that feed turbidity has a major effect on fouling rate. Obviously a very low feed turbidity, of the order of 0.1 JTU or less, is required to maintain satisfactory demineralization for a significant length of time. Fortunately, the

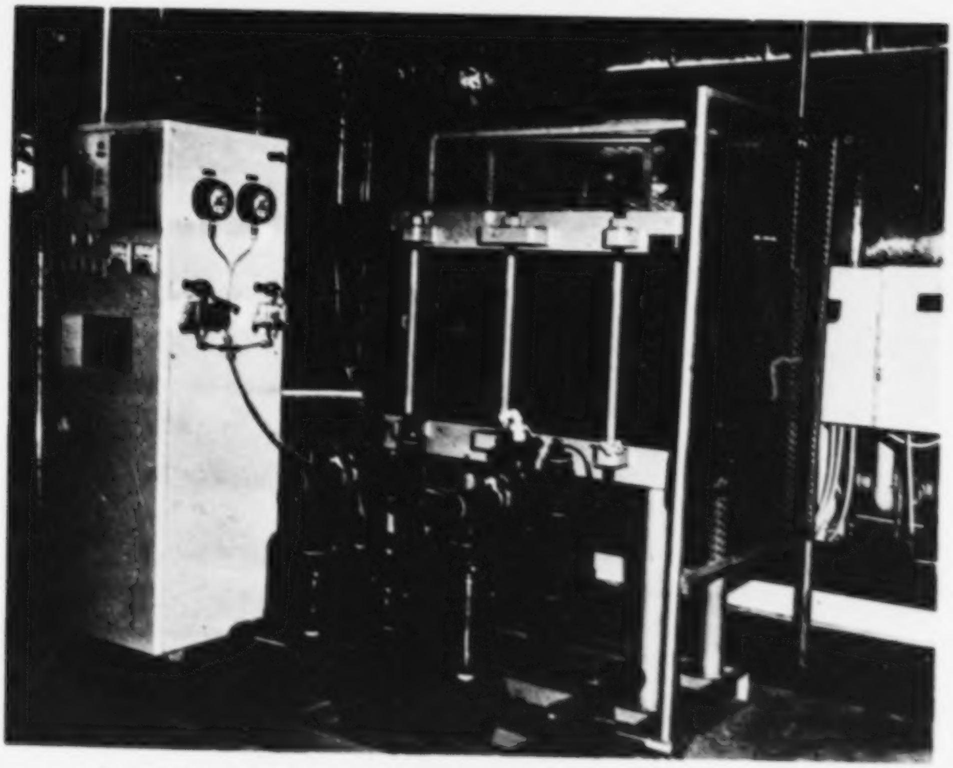


Figure 22. Pilot electrodialysis stack at Lebanon, Ohio. On the right of the skid-mounted unit is the membrane stack itself. Up to 150 cell pairs can be used. On the left is the rectifying equipment for supplying direct current to the stack. In the foreground are dual pumps operating from a single drive. The pump to the left recirculates the concentrate stream; the pump to the right is for feed.

fouling is highly reversible. Most of the fouling materials can be removed merely by shutting down the stack for a day. The middle curve in Figure 23 illustrates the result of stack disinfection by low pH upon fouling. The lower-than-expected fouling rate following acid rinsing of the stack suggests that not only deposition of materials on the membranes but also growth of organisms contributes to fouling. It is believed that fouling can be reduced by using chemical

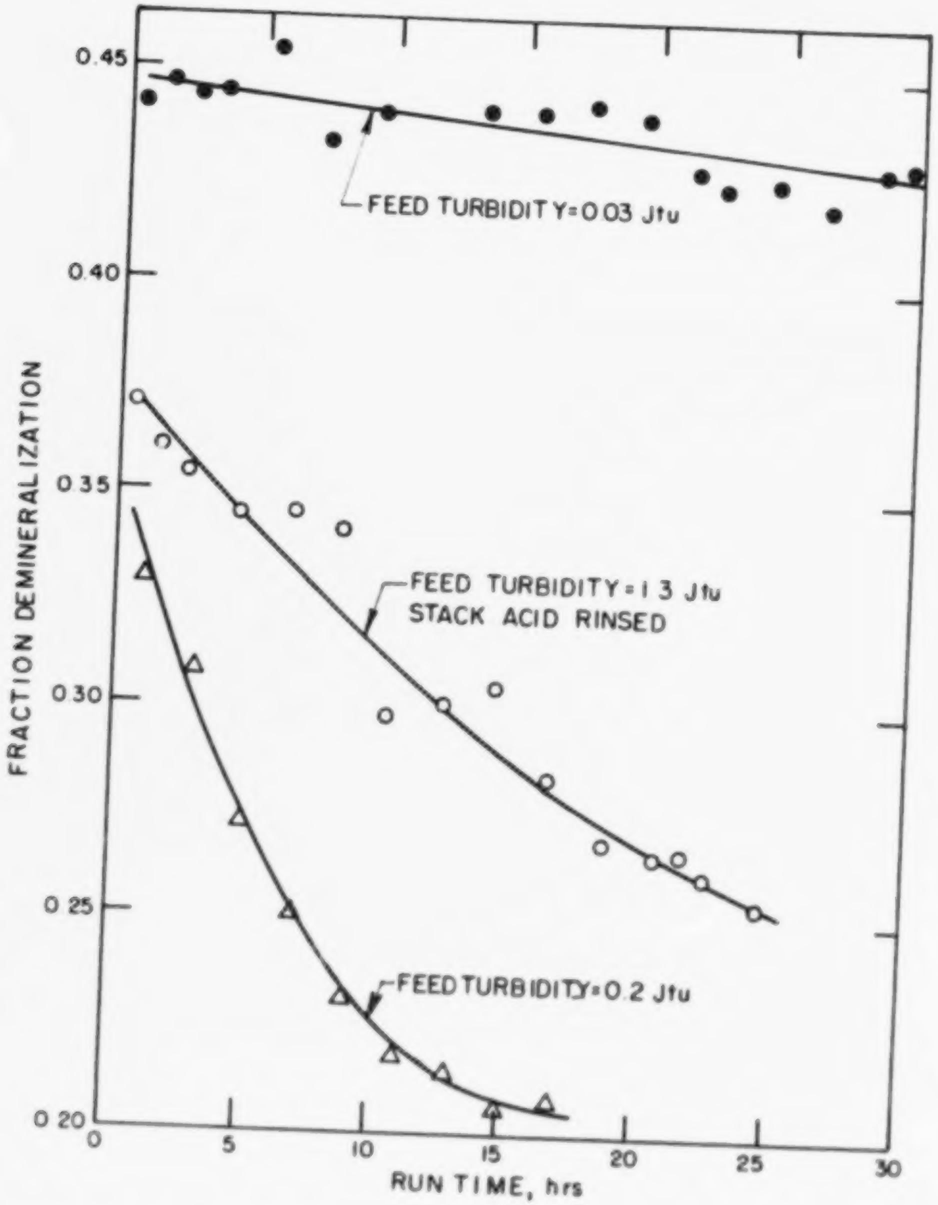


Figure 23. Effect of turbidity on demineralization.

clarification, for example, lime treatment, rather than diatomaceous earth filtration. Chemical clarification equipment has been installed and shakedown begun. Although the resulting turbidity values might not be lower than are obtainable by diatomaceous earth filtration, the composition of the turbidity should be different. Turbidity from an unflocculated secondary effluent is nearly all biological in origin and has a high fouling tendency; turbidity from flocculated water will be a complex mixture of biological material and inorganic floc that hopefully will have lower fouling tendency.

There are methods available that might alleviate stack fouling even with diatomaceous earth filtered water. Two of these are periodic current reversal and the use of turbidity scavenging treatments. These, however, will not be investigated extensively until the effect of chemical clarification is known.

The permanent damaging effect of fouling materials upon the membranes is very small. During 1,500 hours of operation there was only about a 5% increase in membrane pair resistance. Part of the increase is probably due to adsorption of trace soluble organics into the membranes.

Using a waste stream volume that is 9.5 percent of the product stream and keeping concentrate pH less than 5 resulted in occasional calcium carbonate scale formation on the anion membranes. This is not considered a serious problem, however. The particular water studied was high in calcium. Water with less calcium would show less scaling tendency and might even be concentrated significantly more than occurred in this work.

Although fouling has not been completely eliminated as an operating problem, it is felt that electrodialysis is a practical method to partially demineralize wastewater. Periodic stack shutdown, although not desirable, will keep fouling under control. A cost estimate has been made for a 10-mgd plant assuming 15 percent down-time. The capital cost of the plant exclusive of pretreatment should be about $3,400,000. The operating cost exclusive of pretreatment and concentrate disposal should be 16¢/1,000 gal or less.

Future Work

The most important problem that needs study is elimination of membrane fouling. Considerable effort is already underway at the Lebanon Pilot Plant toward overcoming this problem. Chemical clarification might, in itself, reduce fouling. If it does not, other means will be investigated. A study on smaller-scale equipment is planned to determine in greater detail the nature of the fouling and to test possible means of prevention.

Additional information on membrane life and other factors contributing significantly to operating cost will be obtained during continued operation of the pilot unit.

FREEZING

Principal of Operation

When water containing impurities is frozen, the ice formed is of high purity. Freezing of seawater, for example, produces ice of very low mineral content. The same result would be expected from freezing of wastewater.

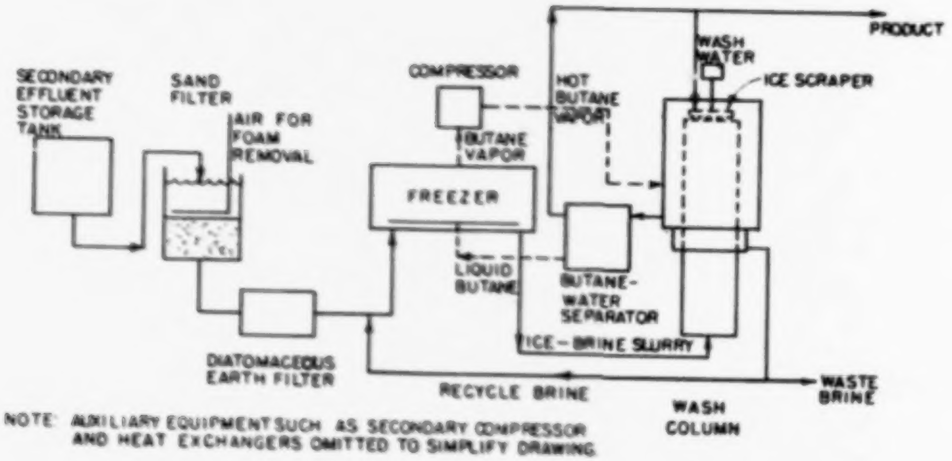
In the process, feed water is cooled and partly frozen. The ice is separated from the unfrozen brine, washed with clean water, and melted to produce purified water. Whenever possible, energy recovery is practiced to decrease treatment cost. Although the process is usually considered a demineralization process, it also is capable of removing organic materials from water. In the wastewater application, a high degree of organic removal would be expected to occur.

Experimental Investigation

Previous work on freezing of wastewater (6) indicated that problems might arise in obtaining high-purity product water. Washing of impurities from the ice crystals, especially organic materials, was different. To investigate the process under more realistic conditions than were possible in bench-scale equipment, a small pilot plant study was undertaken with Struthers Scientific and International Corporation. This company owned, and had operated on seawater, a 750-gpd freezing pilot plant at Oxnard, California. The plant utilized a secondary refrigerant, butane, to remove heat from the feed water. A schematic diagram of the experimental plant is shown in Figure 24. After minor revisions to the pilot plant and a check-out on seawater, the plant was started up on secondary effluent from the Eastside Bio-filtration Plant of the City of Ventura, California. The effluent was filtered through sand and diatomaceous earth and air-stripped to reduce ABS before freezing.

In the first experimental runs, operations were severely hampered by the formation of an over-abundance of very small ice crystals which plugged up the crystallizers. It was felt that this problem could be surmounted by continuous operation until the brine in the crystallizer was concentrated to a TDS of about 15,000 mg/l, but time did not permit such a procedure. To simulate these conditions, rock salt was added to the crystallizer to build up the TDS content. Several runs were made under these conditions. From these runs it was learned that the inorganic salts are more readily washed from the ice than are the organic materials. Organic carbon in the product was about 4 mg/l.

It was estimated from the work that the capital costs for a 10-mgd wastewater renovation plant would be about 10 percent lower than those for a 10-mgd sea water desalting plant. The main reason for this is that a seawater plant would be fed 18 mgd and a wastewater plant 11-mgd or less to produce


SECONDARY EFFLUENT STORAGE TANK
SAND FILTER
AIR FOR FOAM REMOVAL
COMPRESSOR
BUTANE VAPOR
FREEZER
HOT BUTANE VAPOR
WASH WATER
ICE SCRAPER
PRODUCT
LIQUID BUTANE
BUTANE-WATER SEPARATOR
ICE-BRINE SLURRY
DIATOMACEOUS EARTH FILTER
RECYCLE BRINE
WASH COLUMN
WASTE BRINE

NOTE: AUXILIARY EQUIPMENT SUCH AS SECONDARY COMPRESSOR AND HEAT EXCHANGERS OMITTED TO SIMPLIFY DRAWING

Figure 24. Freezing pilot plant.

10-mgd of product-water. At 10-mgd, the total cost of production of pure water from wastewater would be 48¢/1,000 gallons compared to 53¢/1,000 gallons for the seawater plant.

Future Work

A wastewater renovation plant utilizing coagulation, sedimentation, filtration, carbon adsorption and electrodialysis can produce water of higher quality than was obtained in the freezing runs for 25-35¢/1,000 gallons. It seems unlikely that the freezing process could be competitive with this process chain.

No further work is planned for the freezing process at the present time.

ION EXCHANGE

Ion exchange is a well-known method for softening or for demineralizing water. Although softening could be useful in some instances, the most likely application for ion exchange in wastewater treatment is for demineralization. The highly demineralized water usually produced by the process is of higher quality than is necessary, therefore, only part of the total stream need be treated.

Many ion exchange materials are subject to fouling by organics. It is possible, that treatment of secondary effluent for suspended solids removal and possibly soluble organic removal will be required before carrying out ion exchange.

Principle of Operation

Many natural materials and, more importantly, certain synthetic materials have the ability to exchange ions from an aqueous solution for ions in the material itself. Cation exchange resins can, for example, replace cations in solution with hydrogen ion. Similarly, anion exchange resins can either replace anion in solution with hydroxyl ion or absorb the acids produced from the cation exchange treatment. A combination of these cation and anion exchange treatments results in a high degree of demineralization.

Since the exchange capacity of ion exchange materials is limited, they eventually become exhausted and must be regenerated. The cation resin is regenerated with an acid; the anion resin is regenerated with a base. Important considerations in the economics of ion exchange are the type and amounts of chemicals needed for regeneration. Often, water to be demineralized is first passed through a cation exchange material requiring a strong acid, usually sulfuric, for regeneration. The exchange material is called a "strong" acid resin. The amount of acid regenerant is somewhat more than the stoichiometric amount, possibly 100 percent excess of more. If sulfuric acid is the regenerating acid, a waste brine is produced consisting of sulfates of the various cations in the water being treated. Because the partially treated water contains mineral acids, it is common to pass it next through an acid absorbing resin or "weak" base resin. This resin can be regenerated with either a weak or strong base. Efficiency of regenerant use is quite high with these resins. If sodium hydroxide is the regenerating base, a waste brine is produced consisting of the sodium salts of the various anions in the water being treated. Certain anionic materials are not removed by the "weak" base resin and must be further treated with "strong" base resin if thorough demineralization is desired. Regenerant usage by the "strong" base resins is poorer than for the "weak" base resins.

The cost of chemicals required for this typical ion exchange system, although within reason for many applications, is probably too high to make the process generally attractive for wastewater treatment. Some advantage can be gained by carrying out regeneration in a more nearly countercurrent manner than is usually done. A more desirable system, however, would be one in which regenerants could be cheaply recovered and reused. A number of these have been devised and are being developed by resin manufacturers and others. Systems designed for regenerant reuse do not always operate with an acid resin bed followed by a base resin bed.

Experimental Investigations

Regenerant Recovery System - A novel scheme for recovering regenerants was studied by Chemical Separations Corporation. To take advantage of the recovery method, it is necessary to use nitric acid to regenerate the cation resin and ammonium hydroxide to regenerate the anion resin. Upon regeneration of the cation resin, a brine is produced with a high concentration of nitrates. Regeneration of the anion resin produces a brine with a high concentration of ammonium salts. The nitrate solution is evaporated and the residue is steam calcined to produce nitric acid and hydroxides of the metal cations removed from the water. The hydroxides can then be reacted with the ammonium salt solution from anion regeneration to recover ammonium hydroxide.

The critical part of the process from an economic standpoint is the calcination of nitrates to recover nitric acid. Good recovery is required or the makeup nitric acid cost becomes prohibitively high. Nitric acid presently costs about 2.5 times as much per pound as the commonly used sulfuric acid. Laboratory-scale and small pilot-scale runs were carried out to determine the degree of recovery of nitric acid from sodium, potassium, calcium, and magnesium nitrates and mixtures of these. Laboratory work indicated that nearly 100 percent recovery could be achieved for calcium and magnesium at about 600°C, one atmospheric steam pressure, and 1.5 hr calcination time. Under the same conditions, sodium and potassium gave yields less than 50 percent. Rotary calciner pilot runs with less than one hour residence time resulted in considerably poorer yields of acid. In the pilot work it became obvious that carryover of undecomposed nitrate salts into the product was a problem. In view of the incomplete recovery of nitric acid, this part of the regeneration scheme does not appear practical. Furthermore, in all of the work it was assumed that no ammonium nitrate would be in the nitrate brine. If there were any ammonium ion, and this is very likely, it would have to be removed prior to calcination. This removal adds to the complexity and cost of the recovery scheme.

It must be emphasized that the economic feasibility of the nitric acid recovery system depends directly upon the relative costs of nitric and sulfuric acid. With rising sulfur costs, the cost of sulfuric acid has been increasing at a rapid rate. As a result, acid users are giving more consideration to substitutes such as nitric acid. Greatly increased consumption of nitric acid could substantially decrease its cost in relation to the cost of sulfuric acid. If this occurs, further study of the nitrate recovery system may be desirable.

Fouling of Anion Resins - Early anion exchange resins were subject to severe fouling by many organic materials. Significant advances have been made in the elimination of fouling tendencies of some of these resins. It is not well known, however, what effects the soluble and suspended organic materials in secondary effluent may have. A small-pilot-scale survey of a number of anion resins has been initiated to determine fouling effects. Preliminary results are available on one weak base resin, IRA-68.* A sample of this resin was contacted

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**Rohm and Hass Company, Philadelpha*

in a column with sand-filtered secondary effluent for a total of 23 exhaustion cycles. Regeneration was initially carried out in a cocurrent manner with 4 percent ammonium hydroxide. The resin was then converted to the bicarbonate form with water carbonated under a carbon dioxide pressure of 50 psig. For the first 15 cycles there was a gradual decline in exchange capacity, indicating some fouling. About 50 percent of the organics in the feed were removed on the resin. A reduction of ion exchange capacity from 1.0 meq/ml observed for new resin to 0.6 meq/ml occurred. A hydrochloric acid rinse restored the capacity to that of fresh resin. During the remaining cycles no further acid rinse was required to maintain resin capacity. Regeneration for these latter runs was carried out in a direction counter-current to the feed, however, rather than cocurrent with the feed as in the first 15 cycles. It is believed that cocurrent regeneration caused organics initially held in the resin near the column entrance to be moved through the column, resulting in fouling of much of the resin. Countercurrent regeneration, on the other hand, would keep organics on the resin near the column entrance from being moved through the column. Instead, these organics were removed by the regenerant. Analysis of spent regenerant from organic carbon indicated that organic removal from the resin occurred. Using countercurrent regeneration, organic fouling is not a significant problem for this particular resin.

During the study, breakthrough curves for common anions in wastewater were obtained. A high selectivity was found for phosphate and sulfate ions. This result is in line with the rule of thumb that multivalent ions are usually removed preferentially to monovalent ions. Essentially all the resin capacity could be used for removal of these two ions.

Future Work

Work being planned for ion exchange includes study of new regenerant recovery schemes, testing of special resins that can be used in the presence of organics or even as scavengers of organics and testing of resins highly selective for certain specific ions. Selective resins are of special interest for removal of ammonium ion and other nutrients from water. Certain natural zeolites are selective for ammonium ion in the presence of sodium. Since sodium is present in municipal wastewater in large amounts relative to other cations, selective removal of ammonia means a substantial savings in regenerant cost. In the planned study, calcium salts will be tested as regenerants. Development of a practical ion exchange process for ammonia removal would represent a significant advance in wastewater treatment.

REVERSE OSMOSIS

Reverse osmosis is one of the few really new water-treating processes. All the important developments in this process have been made in the last 10 years. Its principal application presently is in demineralization of waters too high in minerals for an intended use. Application of the process is not yet widespread, but interest is rapidly increasing. The reason for the increasing interest is the simplicity of the process, the high product quality, and the low treatment cost that could result from further development work. Although reverse osmosis is usually considered a demineralization process, it also has the capability of removing many of the organic materials in wastewater. Suspended material is almost totally removed.

Principle of Operation

Several types of materials, when formed into sheets, have the property of preventing passage of minerals while allowing the passage of water in which the minerals are dissolved. Reverse osmosis makes use of this special property. The name is derived from the fact that, in the process, water is caused to pass from a solution of higher concentration through a membrane to a solution of lower concentration, the opposite of natural osmosis. To cause this flow, a pressure greater than the osmotic pressure must be applied to the more concentrated solution. In a practical situation, pressure considerably in excess of the osmotic pressure is required for useful water flux through the membrane.

The type of membrane that is presently being used in all reverse osmosis equipment is a specially prepared cellulose acetate. The method of preparation gives a dense layer, less than one micron thick, on one side of the otherwise rather porous membrane. This dense layer is believed responsible for rejecting most of the impurities in the water. The mechanism causing rejection is not completely understood.

High concentrations of the soluble materials rejected by the membranes can build up on the concentrate side causing scale. Suspended material can also build up, forming a fouling layer. Equipment design must, therefore, incorporate means for lowering the concentration of materials at the membrane. This is commonly done by moving water past the membrane surface at a high enough rate to cause turbulence.

Experimental Investigations

An initial investigation by the Aerojet-General Corporation of the treatment of municipal secondary effluent with reverse osmosis indicated that a very high degree of inorganic and organic removal was possible (6, 20). This study showed, however, that decline in water flux through the membrane with time might be a problem. The General Atomic Division of General Dynamics then carried out a study of their own at the Pomona, California Water Renovation Plant. Product quality and flux rate were similar to those obtained in the earlier study. A flux decline was not observed in this investigation. As a result of the General Atomic work, a 5,000-gpd pilot unit was purchased from the company and installed at the Pomona Research Facility. The pilot unit is shown in Figure 25. This equipment has spiral-type membrane packages shown in Figure 26. These packages are made up of several sandwiches of two membranes with a porous backing between. Each sandwich is sealed on three edges and the fourth edge is connected to a collection tube around which the sandwiches are wrapped. A thin screen-like spacer is placed between adjacent membranes to permit turbulent flow of water across the membrane surfaces. Water passes through the membranes into the backing and to the collection tube. A large membrane area can be packed into a small pressure vessel. To prevent formation on the membranes of pH-dependent inorganic scales such as calcium carbonate, the feed stream is acidified.

Mechanical difficulties prevented the taking of meaningful data immediately after completion of installation. After solving the most serious mechanical problems, a run was begun using carbon-treated and chlorinated secondary effluent with pH adjusted to 5. Only a portion of the total membrane area was used in this run. Inlet pressure was 400 psig. The initial flux was about 5 gpd/ft.^{2} To prevent an increase in pressure drop from feed point to brine outlet resulting from the presence of suspended solids, a daily air-water cleaning was employed. A flux decline of about 15 percent occurred during the first 250 hrs of operation. Little further decline was noted until after 1,100 hrs of opera-

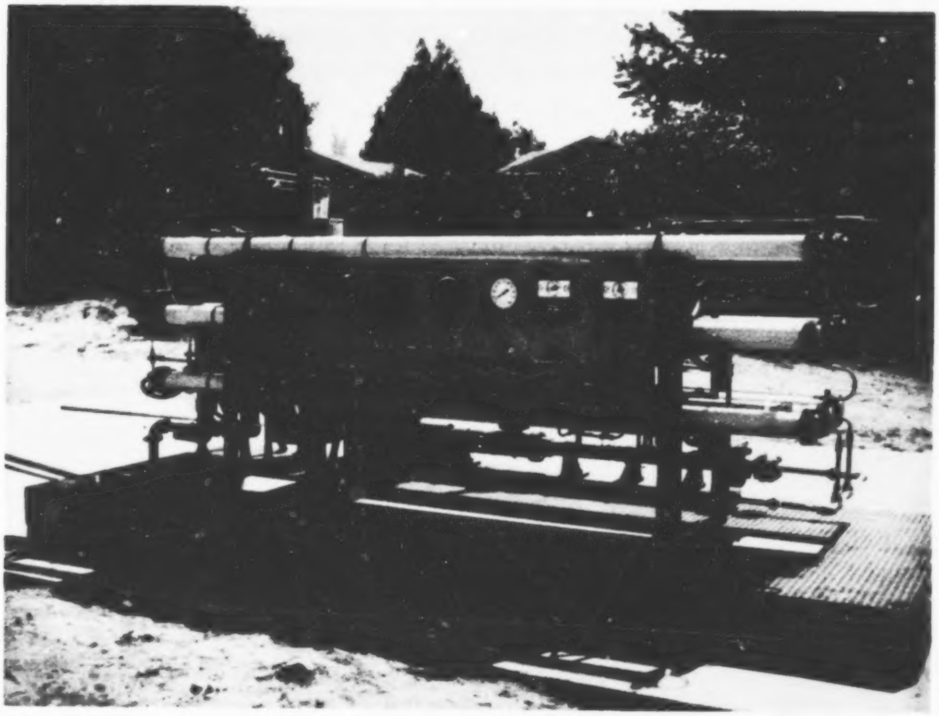

Figure 25. Pilot reverse osmosis unit at the Pomona Research Facility.

tion. Flux decline then continued until the run was terminated after 1,600 hrs. Difficulties with the chlorination system prevented chlorination after 500 hrs. Examination of the membrane support material when the run was terminated indicated growth of mold that is believed to have caused the flux decline. Chlorination of the feed to the end of the run should have prevented the growth. Product quality during the run was excellent. TDS removal was greater than 95 percent. Removal of ammonia, which is known to be poor for reverse osmosis membranes, was greater than 85 percent. The organic content of the product was negligibly small. This is not surprising since the feed was carbon treated and had an average COD of less than 12 mg/l. Further long term runs at higher operating pressure and with secondary effluent that has not been carbon treated are needed to fully evaluate the effectiveness of this unit.

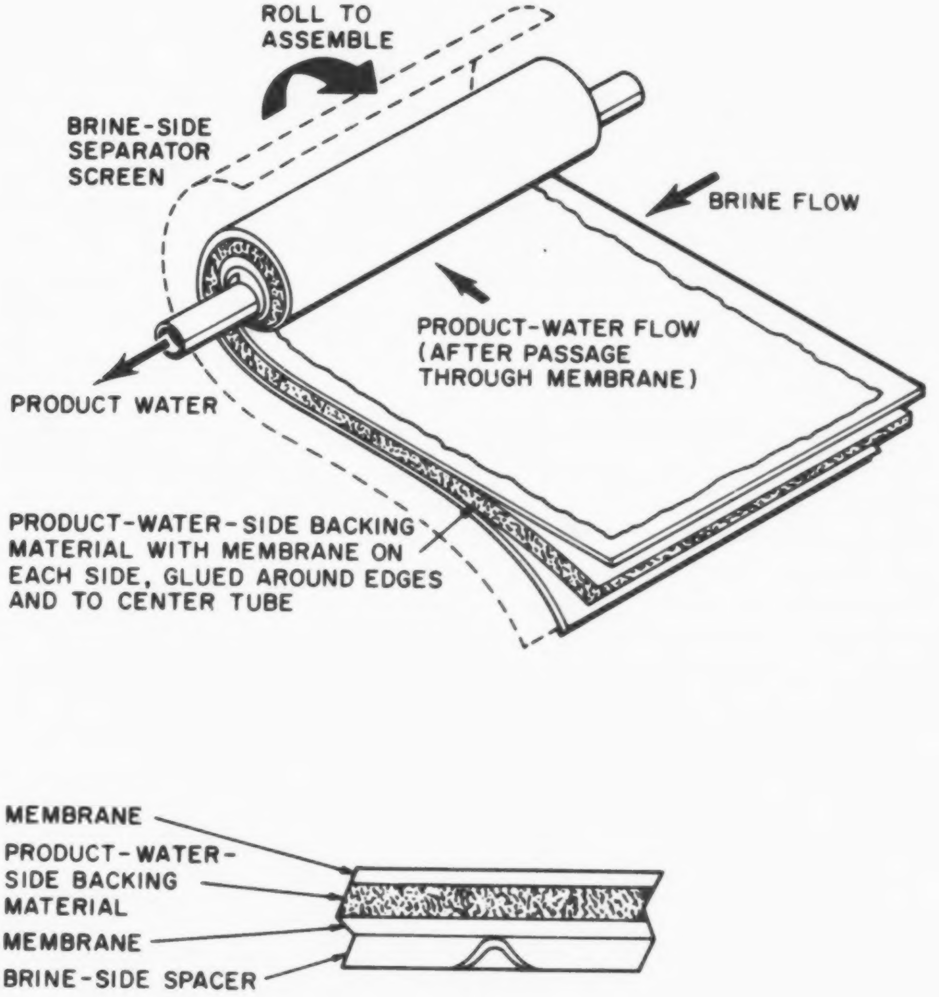
ROLL TO ASSEMBLE
BRINE-SIDE SEPARATOR SCREEN
BRINE FLOW
PRODUCT-WATER FLOW (AFTER PASSAGE THROUGH MEMBRANE)
PRODUCT WATER
PRODUCT-WATER-SIDE BACKING MATERIAL WITH MEMBRANE ON EACH SIDE, GLUED AROUND EDGES AND TO CENTER TUBE
MEMBRANE
PRODUCT-WATER-SIDE BACKING MATERIAL
MEMBRANE
BRINE-SIDE SPACER

Figure 26. Membrane configuration in reverse osmosis pilot unit.

A study of a tubular reverse osmosis unit* was also carried out at Pomona. In this unit, feed water flows inside the tubes and product water collects in a shell that surrounds groups of seven of the tubes. Both secondary effluent and carbon treated secondary effluent were investigated. The feeds were chlorinated and, for the most part, acidified to a pH of 5. Feed pressure was in the range of 700 to 850 psig. Frequent tube breakage and other oparating problems interfered with the experimental program by preventing long runs, but certain information was obtained. It was clearly demonstrated that pH adjustment is necessary to prevent calcium carbonate scale formation. Limited results suggest that membranes treating secondary effluent without carbon treatment undergo more rapid flux decline than when carbon treatment is used. Since extensive studies of effluents with and without carbon treatment are planned, this point will be clarified in the future. Runs with membranes having initial fluxes covering a range from 10.8 to 17.5 gpd/ft.^{2} indicated that the rate of flux decline increases with increasing initial flux. Similar results have been obtained by other investigators on waters other than wastewater. Product water from the tubular unit was low in both inorganics and organics. Removal of TDS was about 95 percent, phosphate 99 percent, and ammonia 87 percent. Nitrate, like ammonia, is removed less effectively than gross inorganics measured by TDS. Nitrate removal was about 68 percent. Removal of organics from the secondary effluent was 96 percent measured as COD. Average product COD was only 1.9 mg/1. Whether these excellent removals could have been sustained for long periods was impossible to determine because of operating problems.

Future Work

Much remains to be learned about treatment of wastewater by reverse osmosis. Pretreatment requirements, membrane fouling rates, and membrane life will be studied on the pilot unit at Pomona. It is known that cellulose acetate will slowly hydrolyze and lose its effectiveness. Future work should, therefore, include development of membranes that do not decompose significantly in water. Although the present membranes remove much of the soluble organics from wastewater, a higher degree of removal may be desirable. Membranes can probably be developed with improved organic removal capability. Membrane configuration is important because of the effect on fouling and scaling. The spiral-type configuration is being tested in the Pomona pilot unit. The flat plate configuration was tested in the initial wastewater work. Plans are to obtain a pilot unit with this configuration for further study. Tubular units other than the Havens equipment are available and will be tested. Other configurations will, no doubt, be developed and will also require investigation.

**Loaned by Havens Industries, San Diego, Calif.*

NUTRIENT REMOVAL

Certain materials in wastewater act as nutrients to algae and other aquatic plants in receiving waters causing excessive growths of these organisms. The excessive growths, algae blooms, are an esthetic nuisance. They also cause wide swings in dissolved oxygen content that may kill fish. Decomposition of the plants contribute organic matter which then depletes the dissolved oxygen in the water below levels necessary for other aquatic life. At the same time, bad tastes and odors are produced.

Although many materials act as plant nutrients, the two most important ones in wastewater are phosphorus and nitrogen. In secondary effluent, phosphorus occurs largely as inorganic orthophosphate ion, but also combined in organic materials. Nitrogen also occurs as inorganic and organic forms. In secondary effluent the inorganic forms constitute the greatest nutrient problem. They are predominantly ammonia or nitrate with minor amounts of nitrite. In most secondary effluents ammonia is the important form. Under certain conditions, an important one being an excess of oxygen, it is possible, however, to convert the ammonia to nitrate biologically. This is called nitrification and the water is termed a nitrified effluent.

Besides its problem as a nutrient, nitrate at high concentrations in drinking water can cause methemoglobinemia in infants. A drinking water standard (21) of 10 mg/l NO_3-nitrogen maximum has, therefore, been adopted in this country. Ammonia exhibits oxygen demand and hence adds to the BOD. Although there is no drinking water standard for ammonia, it can be tasted at a concentration of about 1 mg/l.

Removal methods for phosphorus may be biological or physical-chemical. The biological processes ordinarily remove some phosphorus. By regulating the operation of the activated sludge process there is the possibility that the degree of removal can be considerably increased. Physical-chemical processes include ion exchange and precipitation. Presently, precipitation appears most promising.

Removal methods for nitrate may also be biological or physical-chemical. To make use of the biological method, a highly nitrified secondary effluent must be available. A possible physical-chemical removal method is ion exchange.

Ammonia can be removed during secondary treatment by activated sludge if nitrification is maintained. Nitrifying plants are, however, not common at the present. A physical-chemical method of removal is air-stripping at high pH. A study of this method was made at Lake Tahoe and results were sufficiently promising that a plant-scale installation is planned.

PHOSPHATE REMOVAL BY PRECIPITATION

Principle of Operation

A number of chemicals, including aluminum sulfate and lime, when added to wastewater will precipitate orthophosphate. The precipated material can then be removed by either sedimentation alone or by sedimentation combined with filtration. The reactions that occur during precipitation are not completely understood. The precipitates are not simple aluminum and calcium phosphates. When aluminum sulfate is the precipitating chemical, a complex structure made up of aluminum associated with hydroxyl and phosphate groups appears to be formed. When lime is used, hydroxyapatite is one material likely to be formed. Studies of this material indicate the chemical composition to be $Ca_5OH(PO_4)_3$. It is an interesting fact that the concentrations of calcium and phosphate in wastewater before addition of lime can greatly exceed the maximum values estimated from the solubility of hydroxyapatite.

Experimental Investigations

Data on phosphate removal by precipitation has been obtained during a number of studies of clarification. In one of these studies (10), several secondary effluents were flocculated in 165-gal. batches with lime or alum and filtered through a dual-media filter. Phosphate removals obtained from the clarification tests and results from jar tests are shown in Table 14. Both lime and alum were effective in reducing the phosphate concentration to low levels, sometimes so low as to be undetected. These results are typical of those found also in other studies.

Figure 27 shows how phosphate concentration decreases with increasing alum addition for a particular secondary effluent sample. In taking these data, samples were flocculated and settled, but not filtered. Filtration would give slightly lower phosphate concentrations. At a dose of 300 mg/l, phosphate was decreased to less than 10 percent of its original value. Considerably more alum is required to significantly reduce the phosphate concentration further. A similar curve would be found for lime. The shapes of these curves vary somewhat among different effluent samples.

Future Work

The removal of phosphate with lime and alum is well established. Additional data will, however, be accumulated during operation of pilot-scale clarification units at Pomona, California; Lebanon, Ohio; and Washington, D.C. Laboratory-scale work to determine why phosphate concentration can exceed the theoretical solubility is planned. The answer to this question could lead to new processes for phosphate removal.

Table 14. PHOSPHATE REMOVAL DURING BATCH CLARIFICATION

Chem [a]	Dose (mg/l)	Phos (mg/l) In[b]	Phos (mg/l) Clar
Al	400	--	--
Al[c]	450	58	0.0
Ca[c]	450	58	0.0
Al	300	19	0.8
Ca	303	23	1.0
Ca[c]	133	35	1.0
Ca[c]	151	33	0.4
Al	350	21	0.0
Ca	227	29	0.5
Al[c]	300	24	0.8
Ca[c]	300	24	2.0
Ca	141	20	2.8
Al[c]	150	11	0.0
Ca[c]	150	11	0.4
Ca	378	--	0.2

[a] Ca = lime as CaO; Al = alum as $Al_2(SO_4)_3 \cdot 14H_2O$.

[b] In = input value; Clar = after chemical clarification and filtration.

[c] Indicates Jar tests; not filtered.

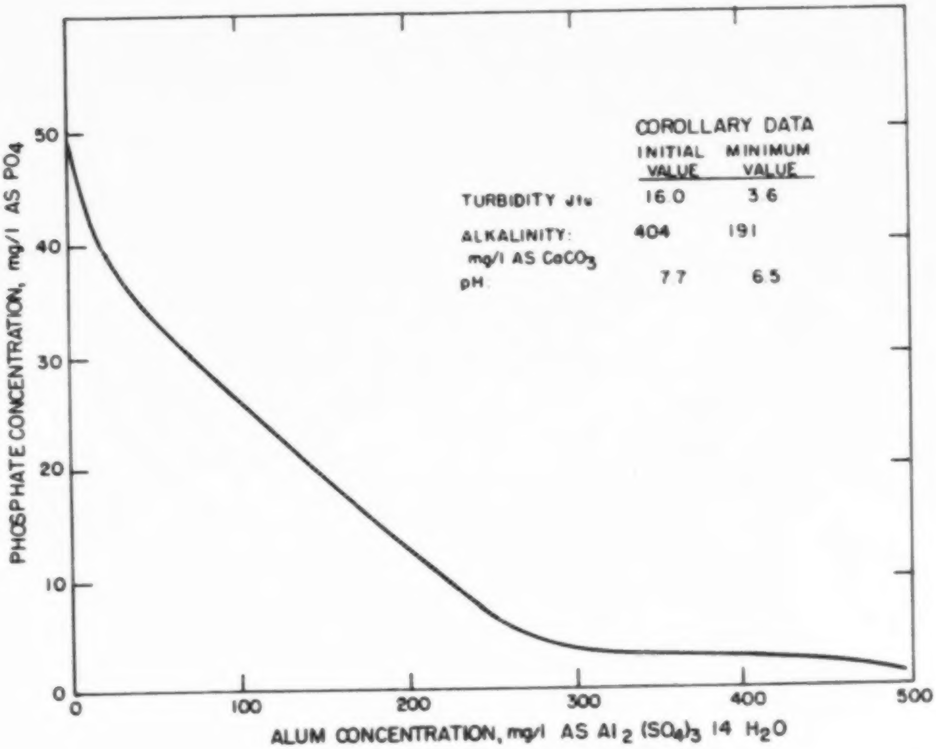

Figure 27. Results of jar tests showing effects of alum dosage on phosphate removal.

NITRATE REMOVAL BY BIOLOGICAL DENITRIFICATION

Principle of Operation

If organic material that can be used for food by denitrifying bacteria is added to a highly nitrified secondary effluent in the absence of oxygen, reduction of nitrate ions to nitrogen occurs. Although the process is a simple one, systems for its application on a large scale remain to be proven effective and reliable.

Experimental Investigations

Two studies of biological denitrification have been undertaken. One of the studies was carried out in conjunction with a small-scale pilot study of the contact stabilization process. The work was carried out at the Mill Creek Treatment Works, Cincinnati, Ohio. A diagram of the system is shown in Figure 28. Nitrification was carried out in a separate aerator following contact stabilization. The denitrification chamber was a separate stirred vessel. Sludge from the settler

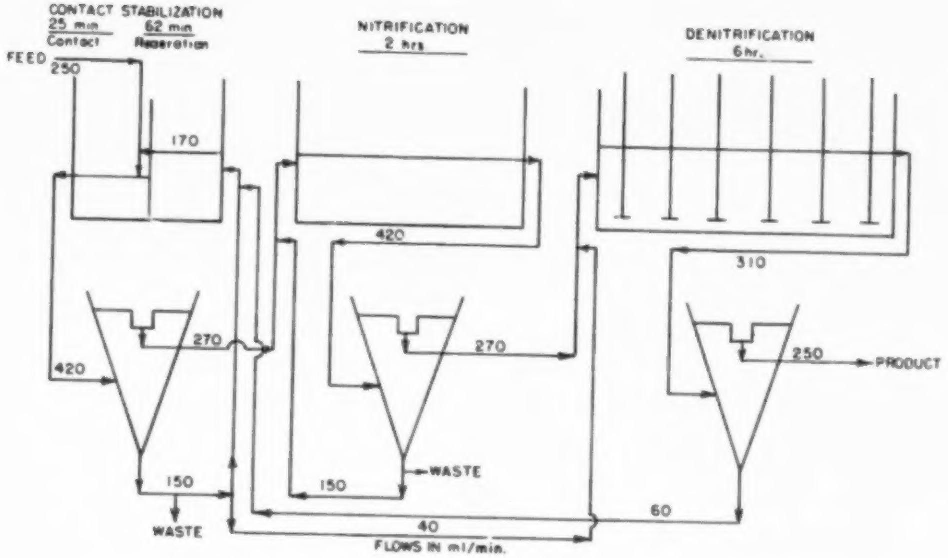
CONTACT STABILIZATION
25 min
Contact
62 min
Reaeration
FEED
250
170
420
270
150
WASTE
NITRIFICATION
2 hrs
420
270
150
WASTE
DENITRIFICATION
6 hr.
310
250
PRODUCT
60
40
FLOWS IN ml/min.

Figure 28. System for nitrification and denitrification.

following the contact stabilization aerator was used to supply organic material to the denitrifying organisms. Over a 4-month period, conversion of ammonia nitrogen to nitrate was 95 percent. Reduction of nitrate to elemental nitrogen averaged 86 percent. The cost of nitrification and denitrification was estimated to be 5 to 6¢/1,000 gal.

A second denitrification study was undertaken at Pomona, California, after it was noticed that a small degree of nitrate removal was occurring in the activated-carbon pilot plant located there. An investigation was begun using a 10-ft long carbon column and methanol as a supplemental food for the denitrifying bacteria. Feed rate is 7 gpm/ft.^{2} Available results indicate that removal of nitrate down to 1 mg/l or less may be obtained with the addition of 2 mg/l methanol for each mg/l of NO_3-nitrogen. Cost of the methanol would be about 2¢/1,000 gal. The organic content of the product-water is not raised significantly by the alcohol addition. More recently, sand has been investigated as a substitute for the carbon. Early results indicate sand may be as effective as carbon for carrying out denitrification.

Future Work

Work is continuing on the study of denitrification on carbon and sand. Successful development of denitrification in packed beds could lead to a very useful process with wide application.

AMMONIA REMOVAL BY AIR-STRIPPING

Principle of operation

Ammonia exists in water either as the un-ionized NH_3 or as the ammonium ion, NH_4^+. While NH_3 is volatile, NH_4^+ is not. The relative amounts of each depend upon pH. At pH of 10 or above, the un-ionized form greatly predominates. Since it is volatile, it can be removed by contacting the water with air. Large quantities of air are required to reach the 1-mg/1 concentration that is considered a maximum for some water uses. Although the pH can be raised in several ways, the most economical method is by addition of lime. The air-stripping process, therefore, would probably be used in conjunction with lime clarification.

Experimental Investigation

Air-stripping of ammonia was studied on secondary effluent at the Pomona Research Facility. Initial work utilized a column packed with plastic Pall Rings. Because of the high pressure drop that develops with this type of equipment, air pumping costs are high. Later work was done using cooling tower equipment. This contactor was about 2 ft high, 3-1/2 ft long, and 3 ft wide and contained 5 ft^2 of wood slats. Secondary effluent with lime-adjusted pH flowed at a steady rate downward over the slats perpendicular to air that was blown horizontally with a fan. Power costs for this equipment are low, but gas-liquid contact is not as efficient as in a packed column. The 2-ft height of the contactor was not sufficient for high ammonia removal. Water that had been treated once could, however, be recycled to give some indication of the effect of an additional 2-ft of tower height for each recycle. This method of multiple contacting was used to obtain the removal results shown for various tower heights in Figure 29. Results are given for two liquid loading rates, 0.88 and 1.3 gpm/ft^2. Air rate was about 1,500 ft^3/min. There is a noticeable effect of pH on removal. For 90-percent removal and for the range of conditions covered, a pH of at least 10 is required. Removal to 1 mg/l, or slightly over 95 percent average, requires a pH of 11 or higher at an air-to-liquid ratio of 350 ft^3/gal. and a tower height of over 20 ft. At 250 ft^3/gal a much taller tower would be required to reach the 1-mg/l level.

Operating at an air-to-liquid ratio of 350 ft^3/gal. and using a 20-ft tower, the total operating cost of the process is about 2¢/1,000 gal. This does not include the cost of lime or solids removal from the product water. For the effluent studied, the lime cost to raise the pH to 9.9 is estimated at about 3¢/1,000 gal. Considerable savings would result if the lime were recovered.

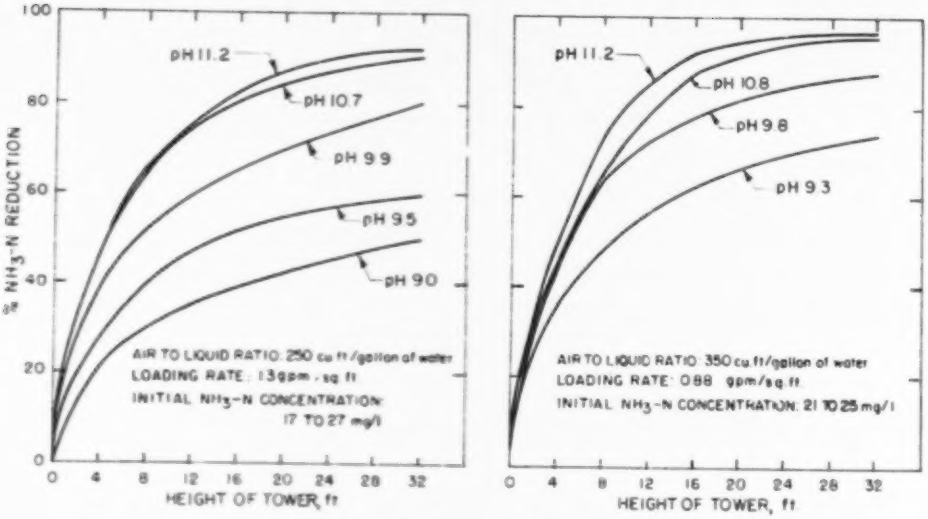

Figure 29. Ammonia-nitrogen reduction-air stripping with pilot cooling tower.

Future Work

The ammonia-stripping process will be tested on a 100,000-gpd pilot scale at the Washington, D.C. Pilot Plant. The study will be made on high-pH water from a lime clarification system.

NUTRIENT REMOVAL FROM OXIDATION POND EFFLUENT

A project (22) has been carried out at Lancaster, California, in coöperation with the Los Angeles County Sanitation Districts to improve the quality of water from oxidation ponds to the extent that it could be used for recreational lakes. It was necessary that the water be of high enough quality to allow growth

Table 15. PROPOSED STANDARDS FOR RECREATIONAL LAKE WATER AT LANCASTER, CALIFORNIA

Turbidity	< 10 JTU
PO_4	2 mg/l
pH	< 8.0
Algae	< 10,000/ml
Coliform & virus	To meet requirements of County Health Officer

The standards were later revised to a PO_4 content of < 0.5 mg/l since this was found necessary to prevent excessive algal regrowth.

and propagation of fish. It has been shown that the ponds would not support fish life, probably because of the low dissolved oxygen concentration occurring during the dark hours when the algae were not producing oxygen. The initial water quality objectives set for the study were those shown in Table 15.

Principle of Operation

Suspended solids and phosphate removal are types of processes required for production of the recreational water. Chemical clarification processes are appropriate and, with large enough doses of lime and alum, good results can be expected.

Experimental Investigation

Studies of various chemical clarification systems were carried out for a period of more than two years on laboratory and pilot-scale units. Laboratory studies included jar test evaluations of coagulants to determine the most effective coagulant and coagulant aid, their required dosages and relative costs. The results of the laboratory studies are shown in Figures 30 and 31. Figure 30 shows that alum is the best over-all coagulant for reducing turbidity. Figure 31 compares the efficiency of lime and alum in removing the phosphate ion.

Several pilot-scale pieces of equipment ranging in capacity from one to 25 gpm were evaluated on the site. These included an upflow clarifier, a high

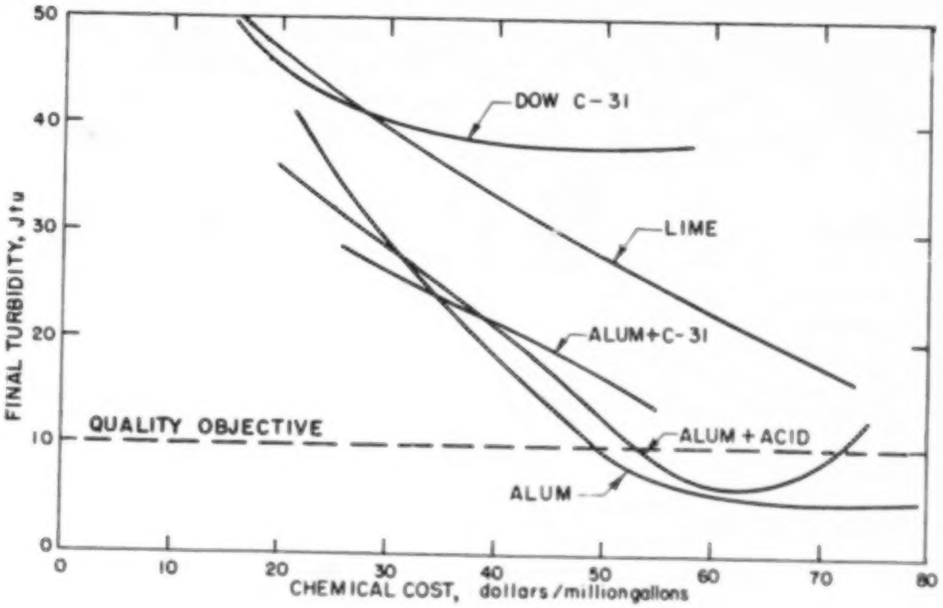

Figure 30. Cost versus final turbidity for different coagulants. Laboratory jar tests.

density solids clarifier, a dissolved air flotation unit, a sedimentation tank and sand and diatomaceous earth filters. Of all those tried, the best series of processes was found to be similar to that used in water treatment processes; that is, a rapid-mix section for coagulating chemicals followed by flocculation, straight sedimentation, dual-media filtration, and chlorination. Alum was the chemical selected for coagulation. The effect of alum dosage in the pilot equip-

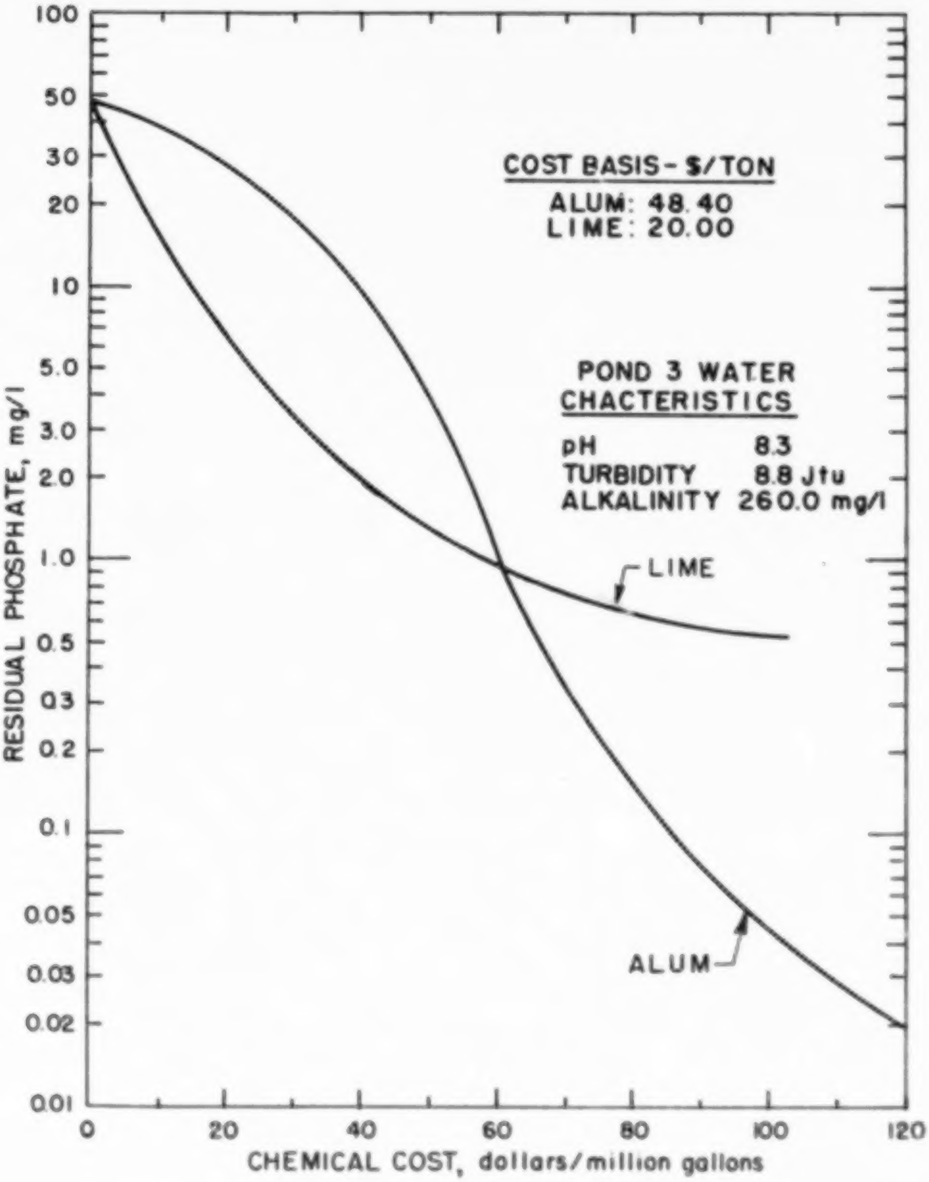

Figure 31. Residual phosphate for alum and lime coagulation. Laboratory jar tests.

ment is shown in Figures 32 and 33. Table 16 shows the quality of water produced by the process. It has been demonstrated in simulated recreational lakes at the Lancaster site that this water will not produce algal blooms and will retain enough dissolved oxygen to propagate fish.

A 500,000-gpd plant is being designed by Los Angeles County to produce water for 19 acres of recreational lakes that will provide boating, fishing, and picnic areas. At this capacity, the estimated operating cost of the water renovation facility is 18.4¢/1,000 gal. At 3 mgd, the total output of the oxidation ponds, the estimated operating cost is 15¢/1,000 gal.

Table 16. COMPARISON OF OXIDATION POND AND CHEMICALLY CLARIFIED WATER CHARACTERISTICS

Characteristics	Pond Water	Product Water
pH	8.3	6.7
Turbidity (JTU)	90	4
Total Alkalinity (mg/l as $CaCO_3$)	260	95
Hardness (mg/l as $CaCO_3$)	80	100
Suspended Solids (mg/l)	75	6
Dissolved Solids (mg/l)	575	575
Chemical Oxygen Demand (mg/l)	250	50
Biochemical Oxygen Demand (mg/l)	38	< 10
Dissolved Oxygen (mg/l)	0.1 to 40	7 - 15
Ammonia-N (mg/l)	0.1 - 20	0.1 - 20
Organic - N (mg/l)	7 - 20	1 - 3
Nitrate - N (mg/l)	1 - 4	1 - 4
Nitrate - N (mg/l)	0.1 - 12	0.1 - 12
Total - Nitrogen (mg/l)	7 - 20	3 - 20
ABS mg/l	3	3
Phosphate (mg/l)	40	0.25
Algae (Counts/ml)	200,000	7,000
Confirmed Coliform (MPN/100 ml)	7,900	< 1.8
Chlorine Residual mg/l	-	0.2 - 0.5

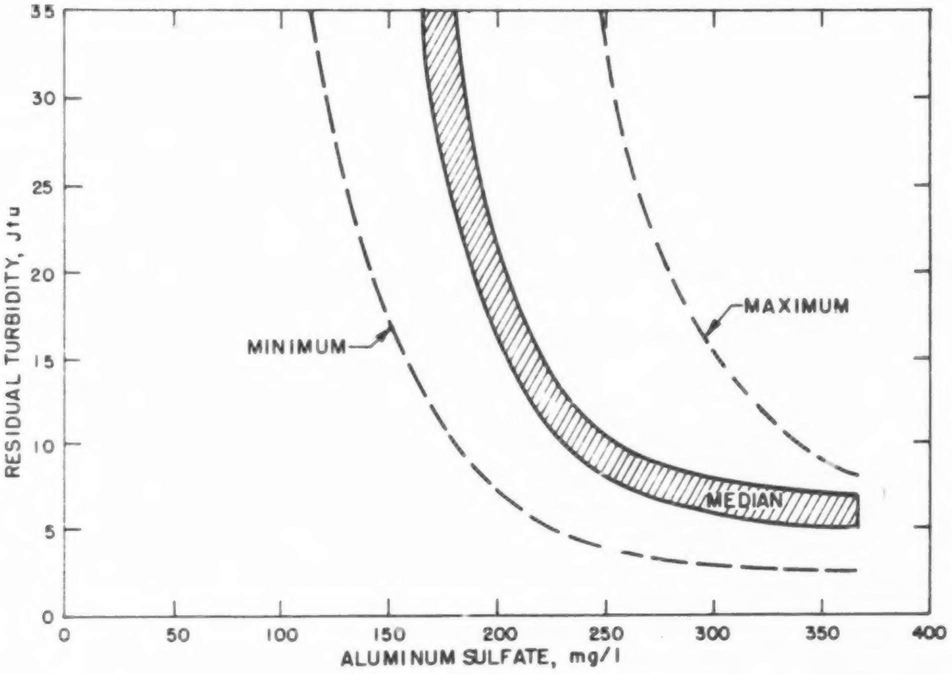

Figure 32. Residual turbidity versus aluminum sulfate prior to filtration. Pilot plant.

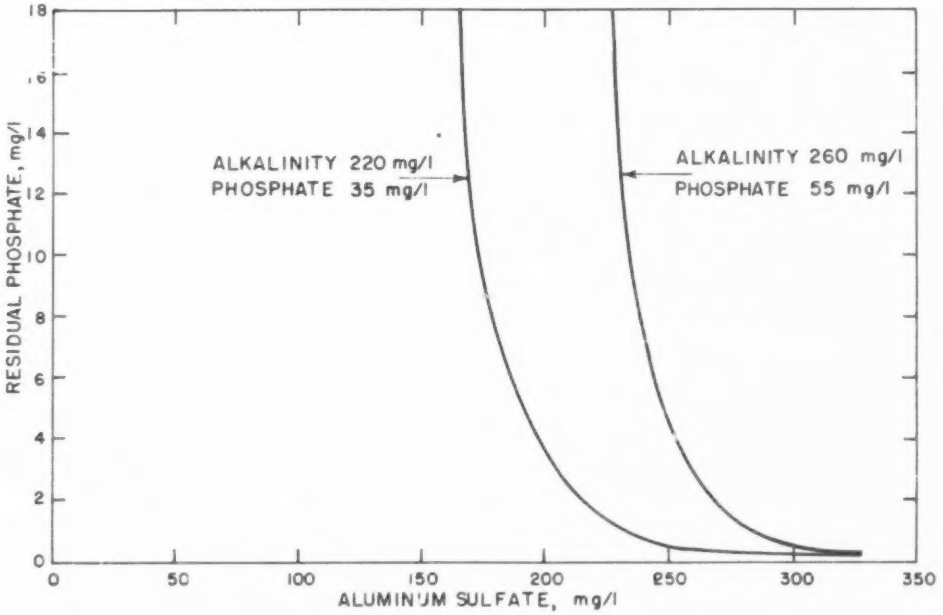

Figure 33. Residual phosphate versus aluminum sulfate prior to filtration. Pilot plant.

ULTIMATE DISPOSAL

Many advanced waste-treatment processes produce a waste stream in which the pollutants removed from the treated water are concentrated. The concentrated stream is a minor, but not insignificant, fraction of the total flow. This waste concentrate must be treated, handled, or placed in such a manner that it no longer pollutes the environment. Its disposition has been termed "ultimate disposal".

Because of the need to prevent further pollution, only a limited number of solutions to the disposal problem are available. These include storage in sealed subsurface cavities or isolated surface ponds, disposal to the ocean in such a way that the seawater will dilute the waste to harmless concentrations, and conversion to innocuous or useful materials. Conversion to innocuous forms is the method often applied to the sludges from conventional treatment processes. These sludges are either digested and dried, or incinerated. The dried sludge or ash is then used for land fill.

Study of many advanced waste-treatment processes has now reached the stage where fairly reliable information is available on the volume and nature of the resulting waste. It can be determined, therefore, which processes present the greatest ultimate disposal problem.

Suspended solids removal processes generally should produce small volumes of waste. Mechanical screening processes such as microscreening, when used on secondary effluent, produce essentially no waste for disposal since solids and backwash water can be returned to the treatment plant. There would be a slight increase in the amount of sludge from primary and secondary treatment. Diatomaceous earth filtration wastes could be treated similarly to those from micro-screening. It might be necessary or desirable to dispose of some or most of the diatomaceous earth separately. The result would be a concentrated slurry of small volume. Chemical treatment processes for solids removal ordinarily produce a sizable volume of waste. In an advanced treatment system, this volume would be significantly reduced by recirculating backwash water through primary and secondary treatment, and, hopefully, by recovering chemicals for reuse from the sludge that is formed during treatment. The material remaining for disposal would be the waste from the chemical recovery treatment and should be less than 1 percent of the feed. Insoluble precipitates containing phosphate would be a component of this waste.

Organic removal processes under study produce little or no waste for ultimate disposal. To make adsorption on activated carbon practical, the carbon must be recovered and reused. There is essentially no disposable waste. It might be necessary, however, to purge a small amount of carbon from the system to prevent ash buildup from repeated thermal reactivation. This waste could be recycled through primary and secondary treatment where it would add slightly to the sludge produced. Not enough is known of oxidation processes to accurately assess the volume or nature of wastes produced. The amounts would not be expected to be large enough to cause a significant problem.

Those processes usually thought of as inorganic removal processes, in contrast to the solids removal and strictly organic removal processes, produce significant amounts of waste. Examples are electrodialysis, reverse osmosis, and distillation. Because of scaling problems, it is impossible during treatment to concentrate the wastes in a small volume. Probably 5 percent and in some cases as much as 10 percent of the feed must be discarded. For electrodialysis the waste stream will probably be clarified, have low organic content and probably contain not more than 5,000 mg/l total dissolved solids. Unless clarification and organic removal were required for the feed to other inorganic removal processes, the wastes will contain, in addition to minerals, suspended solids and soluble organics.

Consideration of the wastes from the various advanced treatment methods serves to point out the almost obvious fact that these wastes can be divided into concentrated sludges of relatively small volume and dilute suspensions or solutions of large volume. The sludges are likely to be the digested or undigested waste from conventional treatment mixed with waste from an advanced process. Some differences in the methods of disposal that apply to the two broad categories of waste might be expected.

Desk-top studies have been made of a number of disposal methods by Louis Koenig-Research to determine approximate costs. Included were incineration with disposal of ash (23), wet oxidation (23), injection into underground strata (24), placement in underground cavities (24), and surface spreading (24). More recently, a study was made of the cost of conveying waste with the intention that the waste would be dumped in the ocean. A summary of conveyance costs for rail, trucking, and pipeline are given in Figure 34. Costs from this figure do not include transporting the waste from the shore out into the ocean. Assuming that a 30-mile outfall would be sufficient, an estimate of this cost can be made for pipelines by adding 70 miles to the distance.

Not all the disposal methods studied are practical and some do not completely fulfill the requirements for ultimate disposal. Wet oxidation removes a large fraction of organics from a waste, but only partially reduces total volume and does little to inorganics. Injection underground, to be useful, requires appropriate geological formations, usually the sedimentary types. Figure 35 shows the distribution of these formations in the United States. Obviously, certain sections

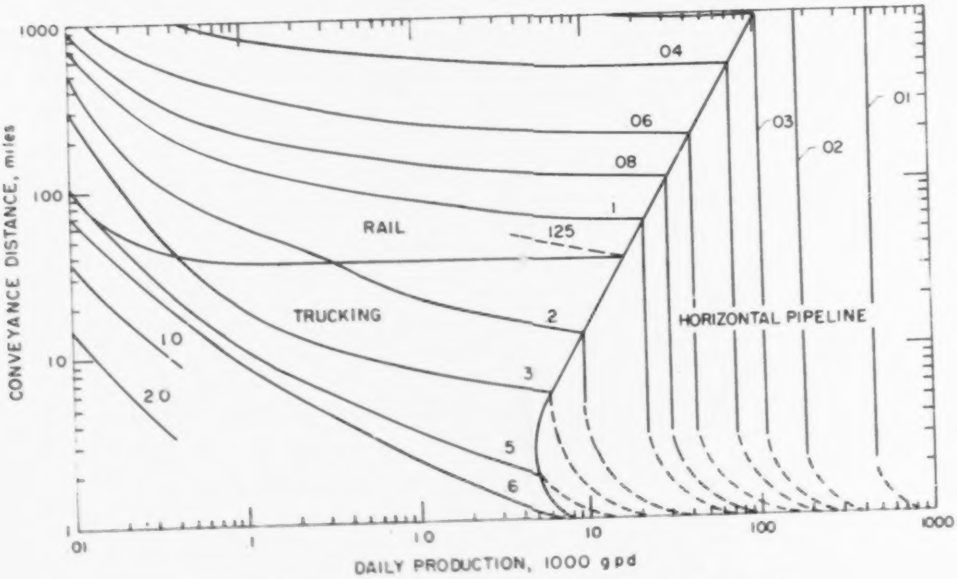

Figure 34. Cost surface for conveyance: Pipeline, Truck and Rail ($/1,000 gal-mi).

of the country could not depend on injection. Placement in underground cavities other than those formed by nuclear explosion does not appear practical. So little information is available on nuclear cavities that these cannot be given strong consideration at this time. Surface spreading could only be considered ultimate disposal if the waste were completely innocuous.

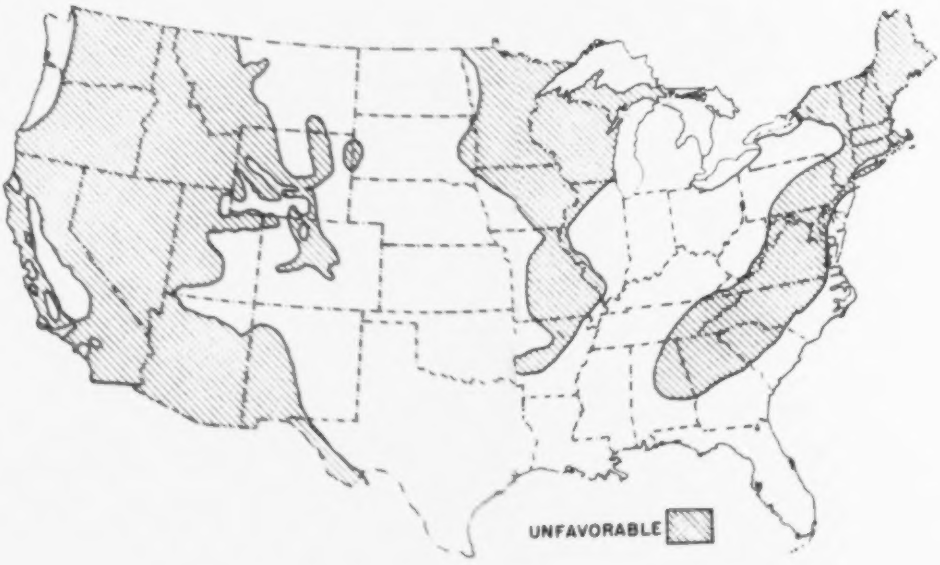

Figure 35. Areas of potential injection sites (sedimentary basins).

If either of the two general categories of wastes are considered separately, certain disposal methods become impractical. For concentrated wastes of low volume, injection probably would not be feasible because of the presence of a large amount of insoluble material. Remaining complete disposal methods are then, incineration with conveyance of ash to the sea, or direct conveyance of the waste to the sea.

For the case of a 100-mgd plant with 0.5 percent waste by volume, disposal costs per 1,000 gal. of product-water would be about 2.5¢ for incineration without disposal of the ash. Direct disposal of the waste to the sea without incineration would be less than 1¢/1,000 gal. of product for 100-mile conveyance and about 5¢/1,000 gal. for 1,000-mile conveyance. Considering that a conveyance cost for the ash must be added to the incineration cost, there is not a clearcut difference between the costs for the two methods. These figures give some idea of the cost that would be involved in complete disposal of a relatively concentrated low-volume waste. If wet oxidation was all the treatment necessary, it could be done at slightly lower cost than incineration. Spreading would be very cheap, less than 0.1¢/1,000 gal.

Of the complete disposal methods studied, those that might be applied to large-volume, dilute waste are incineration, injection underground, and conveyance to the sea. Incineration must be preceded by extensive preconcentration, assumed to be by distillation. Costs reported for incineration (23) include this preconcentration. In estimating preconcentration cost, however, scaling was assumed to be less of a problem than it probably will be. The reported total incineration costs are, therefore, probably low for dilute wastes. Disposal to the sea without incineration might also involve a preconcentration step for lowest total cost. Again the scaling problem will be an important consideration.

Table 17 gives disposal costs by conveyance to the sea for some typical situations in which a dilute waste is produced. Data for the table were taken from Figure 31 and unpublished information from Louis Koenig-Research. For distances of 1,000 miles, preconcentration is necessary for lowest cost. It should be pointed out, however, that preconcentration costs are in doubt and might actually be considerably higher than assumed. It is also possible that if preconcentration were carried to the degree indicated, the product could contain enough precipitated material to be unpumpable. The most important conclusion to be drawn from Table 17 is that ultimate disposal to the sea of the large volumes of waste from inorganic removal processes is expensive unless the distance is very short. Dr. Koenig has proposed combining the wastes from a number of cities, "group disposal", to improve the cost picture. More dependable cost figures for preconcentration are necessary, however, before any definite statements can be made of the minimum possible cost of conveyance to the sea.

Table 17. EFFECT OF DEGREE OF WATER RECOVERY ON COST OF ULTIMATE DISPOSAL TO THE SEA

Disposal Method: Preconcentration (If Economical), Conveyance, 30 Mile Ocean Outfall

Plant Size, MGD		10				100			
Percent Recovery		95		90		95		90	
Waste Produced, 1000 gpd		500		1000		5000		10000	
Total Solids Concentration Ⓐ mg/l		11000		5500		11000		5500	
Conveyance Distance, miles		100	1000	100	1000	100	1000	100	1000
Preconcentration to Solids fraction = 0.55 Ⓑ		-	Economic	-	Economic	-	Economic	-	Economic
Volume to be Conveyed, 1000 gpd		500	10	1000	10	5000	100	10000	100
Cost for Preconcentration	$/day	-	900	-	1400	-	6000	-	7000
Cost for Conveyance	$/day	500	310	750	310	2200	3000	2900	3000
Conveyance Mode	-	Pipe	Rail	Pipe	Rail	Pipe	Pipe or Rail	Pipe	Pipe or Rail
Cost for Ocean Disposal	$/day	420	170	560	170	1400	220	2400	220
Total cost	$/day	920	1380	1310	1880	3600	9220	5300	10220
Percent savings in Preconcentration		-	74	-	76	-	61	-	68
Cost per 1000 gal Product water		9.7	15	15	21	3.9	9.7	5.9	11

Ⓐ Assumes 550 mg/l total solids in feed - 50 mg/l organics and 500 mg/l inorganics

Ⓑ Preconcentration to a solid fraction = 0.1 was found to be uneconomical in comparison to 0.55

For one of the cases given in Table 17, 100 mgd with 95-percent recovery, disposal costs for incineration and injection have been calculated. These are respectively 4.8 and 0.9¢/1,000 gal. product-water. The incineration cost does not include conveyance of ash to the sea. It is also subject to doubt because of possible error in the cost of preconcentration. Incineration appears to be more expensive than direct conveyance of waste to the sea when the distance is about 100 miles, but should be less expensive than direct conveyance for long distances. Injection is significantly less expensive than the other two methods. It should be the method of choice in any locations where the geology is satisfactory.

Future Work

The ultimate disposal studies conducted in the past were undertaken to obtain a broad perspective of possible methods and approximate costs. No attempt was made to demonstrate by experiment the technical feasibility of the methods. Treatments used on the wastes from conventional sewage treatment were not included because their costs were already established. Now that most available disposal methods have been surveyed, it is necessary to conduct detailed studies of those that appear promising.

One point demonstrated by past studies is the high cost of conveying wastes long distances to the sea. Disposal methods such as conversion of waste to useful and innocuous forms deserve extensive investigation since they will reduce or eliminate the need for conveyance. Obvious applications for reuse of the waste include recovery of coagulating chemicals from clarifier sludges and reactivation of exhausted carbon. Presently the dried, digested sludge from conventional waste treatment is sometimes used as a soil conditioner and low-grade fertilizer. Incineration of advanced treatment wastes may in some cases produce a sufficiently harmless residue that disposal as land fill will be satisfactory. This point needs further exploration. In many sewage treatment plants today, sludge is incinerated and the ash is disposed of as land fill.

Unless a waste can be concentrated to a very small volume, the use of conveyance is unrealistic. For the dilute wastes from inorganic-removal processes, where conveyance may in some cases be the only available disposal method, extensive preconcentration is a necessity. Technically, preconcentration is possible. Experimental work is required, however, to determine which types of equipment are practical. Scaling and fouling problems could be severe.

Injection of wastes into the ground is an economically promising disposal method. Little study has been made, however, of the pretreatment requirements for the waste to be injected. Colloidal and soluble organic contaminants could plug the porous rock formations. Inorganic materials in the waste might be incompatible with the strata, also causing plugging. Investigation of these problems is required.

It is likely that conventional sludges will, in the future, contain wastes from advanced processes that have been recycled through the conventional processes. The effect of the added wastes in these sludges requires study. Present disposal methods for wastes from conventional treatment plants are not always satisfactory. Study of ways to get rid of these wastes in a manner that better fulfills the definition of ultimate disposal would be desirable.

PRACTICAL STATUS OF ADVANCED WASTE TREATMENT

A number of advanced waste treatment processes are sufficiently well developed that they might be, or are being, applied on a large scale.

Chemical clarification using lime or alum appears practical for suspended solids removal and phosphate removal from secondary effluent. Granular activated carbon treatment is practical for removal of soluble organic materials from secondary effluent. The application of both chemical clarification and carbon treatment to primary effluent has been considered, but not enough evidence is available to judge the feasibility. Ammonia removal by air-stripping at raised pH is economically feasible when combined with lime treatment. Denitrification on carbon or sand appears promising for removal of nitrogen from nitrified effluents. This list is sufficient to indicate that there are presently methods available for improving greatly the quality of wastewater.

A discussion of sites where advanced treatments and water renovation are being carried out on full scale was included in an earlier "Summary Report" (6). It is not intended that the earlier discussion be repeated here. There have been some recent developments, however, that, if successful, should be of great value in promoting the use of advanced waste treatment methods.

The most significant use of advanced treatment is at South Lake Tahoe, California. Chemical clarification of the secondary effluent, followed by granular activated carbon treatment, is already being carried out at 2.5 mgd and plans have now been made to expand the capacity of the facility and to increase the degree of treatment. Included in this new 7-½-mgd installation will be two-stage lime clarification with air-stripping of ammonia between stages followed by carbon treatment. Sludge from the clarification process will be calcined to recover lime. Carbon will be reactivated. The high-quality product water will not, for the present, be returned to Lake Tahoe. It will be used to feed another recreational lake and for irrigation.

At Santee, California, secondary effluent is being used, after some additional treatment, to feed a series of man-made recreational lakes. Plans have now been made to improve the treatment of the water before entering the lakes. A 2-mgd conventional treatment plant will be followed by biological denitrification, chemical clarification for removal of phosphate and suspended solids, and chlorination. Smaller-scale pilot studies will include carbon treatment, ion exchange, and electrodialysis.

The injection of wastewater along seacoasts to act as a barrier against seawater intrusion and to supplement the underground fresh-water supply is of increasing interest. At Orange County, California, secondary effluent from a trickling filter is being alum-clarified and chlorinated for injection in a test well. On a small scale, electrodialysis and reverse osmosis are also being tested. At Nassau County, New York, it is planned to treat 400 gpm of activated-sludge secondary effluent for injection. Included in the train of processes will be alum clarification with dual-media filtration, granular activated carbon treatment with reactivation of carbon, degasification with sodium sulfite, and chlorination.

These examples are not meant to be a complete list of all instances of advanced waste treatment or wastewater reuse. At many other sites, advanced processes are being tested or demonstrated on large scale. Much of this work is being partly supported by grants from the Federal Water Pollution Control Administration. Processes being tested range from improved biological treatment to demineralization.

The previous discussion should not suggest that the goals of advanced waste treatment have yet been reached. The locations in which advanced waste treatment is being applied still are few in number. The processes that are being used are limited in variety and contaminant removal capability and usually have had extensive development in another application. They are not necessarily optimized for use with wastewater. Chemical clarification is a good example. This process has had a long history of use in the treatment of surface water to produce drinking water. As presently being used for wastewater treatment, it will remove only suspended material and phosphate. While this removal capability represents a major improvement over secondary treatment alone, the process does not produce pollution-free water and it is not without significant added cost. Some of the cost could be saved if chemical treatment and secondary treatment could be combined. This cheaper combination might have much wider appeal than the two processes in series. Contaminant removal might be improved by adding materials to the water other than those which are usually used for surface water treatment. Much remains to be learned about this relatively well-developed process.

Considerable interest has developed in the increased removal of soluble organics from wastewater. Although several treatment methods have been, and are continuing to be investigated, adsorption on activated carbon appears most practical. Because of the ability to be reactivated quite easily, granular carbon has received more attention than powdered carbon and granular carbon treatment is presently the cheaper method. Continuing work on both granular and powdered carbon should improve the economics of the two treatment methods and possibly make the two competitive.

Nutrients are now recognized as serious pollutants and their removal is receiving increased attention. Phosphate removal can be accomplished by chemical treatment. However, other and possibly cheaper, means for removal are desirable. Nitrogen removal methods, whether they be for ammonia or nitrate, are of major importance. Ammonia removal by air-stripping can only be applied conveniently in combination with lime treatment. A removal method such as selective ion exchange would be desirable. Nitrate removal presently can only be carried out practically by biological means. Physical-chemical removal methods would be of value. Again, selective ion exchange might provide an answer to the problem. Considerable effort will be required to provide efficient nutrient removal methods.

Removal of gross inorganics from wastewater is not yet of widespread interest. Interest will increase, however, as the degree of reuse increases. In locations where water injection is being considered, the need for a means of partially demineralizing the injection water is recognized. At Orange County, California, for example, some demineralization studies are being made. Electrodialysis presently appears to be the most practical method for removing the increment of minerals added during use. Ion exchange may be competitive, but requires further testing. Reverse osmosis is another demineralization method that might be practical. The process has the added advantage of removing organics and suspended material, however, it is too early to determine the feasibility of this general removal treatment.

While discussing the status of advanced waste treatment, one must not forget the many undeveloped methods that remain to be investigated. New treatment methods are constantly being suggested. Many of these will not prove feasible. There is always the chance, however, that a truly novel and valuable process will be discovered that will improve or even revolutionize wastewater treatment.

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APPENDIX

COLLOIDS IN SECONDARY EFFLUENT

Suspended matter, according to the definition in Standard Methods (1), includes everything collecting on a filter membrane that will retain bacteria. Commercial membranes having a maximum pore diameter of 0.45μ are usually specified when a bacteria-retaining filter is required. The Gooch asbestos pad, alternatively used as a filter for suspended solids, has approximately the same maximum pore size. Although material passing through 0.45μ pores is sometimes referred to as "soluble", this term should be reserved for substances in true solution which are dialyzable. Cellophane membranes having an effective pore diameter of about 2.5 mμ and retaining proteins and larger colloidal matter are convenient for dialysis. The range of sizes between 0.45μ (450 mμ) and 2.5 mμ includes colloidal matter. Electron microscope studies (2) have shown that the principal colloidal matter in the effluent from an activated sludge plant consists of fragments of bacterial cell walls. Viruses, phage, flagella and other cellular debris are present to a lesser extent. Figure 36 shows highly magnified cellular debris. The cell wall fragments are thin flexible films about 10 mμ thick and 50 to 500 mμ across. They seem diabolically designed to clog filters and foul the surfaces of heat exchangers and electrodialysis membranes. Membrane filters remove much of the material which mathematically could pass through the pores, presumably by adsorption on the surfaces of the membranes.

Clarification by the formation of a gelatinous chemical precipitate effectively removes organic colloids from wastewaters. Chemicals so far studied include lime, which forms calcium carbonate and gelatinous magnesium hydroxide at pH 11, ferric salts which form ferric hydroxide, and alum which forms aluminum hydroxide.

The role of colloids in the operation of carbon adsorption columns has been considered. The diffusion of a particle 1μ in diameter to the surface of a carbon particle in a typical granular carbon adsorption column should require nearly 10 hours; a 0.1μ particle would require nearly one hour. Experimentally it has been found that only half of the turbidity is removed by 11 feet of 10 x 30 mesh carbon. The organic matter penetrating a carbon column fed with unclarified secondary effluent is apparently largely colloidal in nature since clarification reduces the unadsorbed organic matter to undetectable levels (3).

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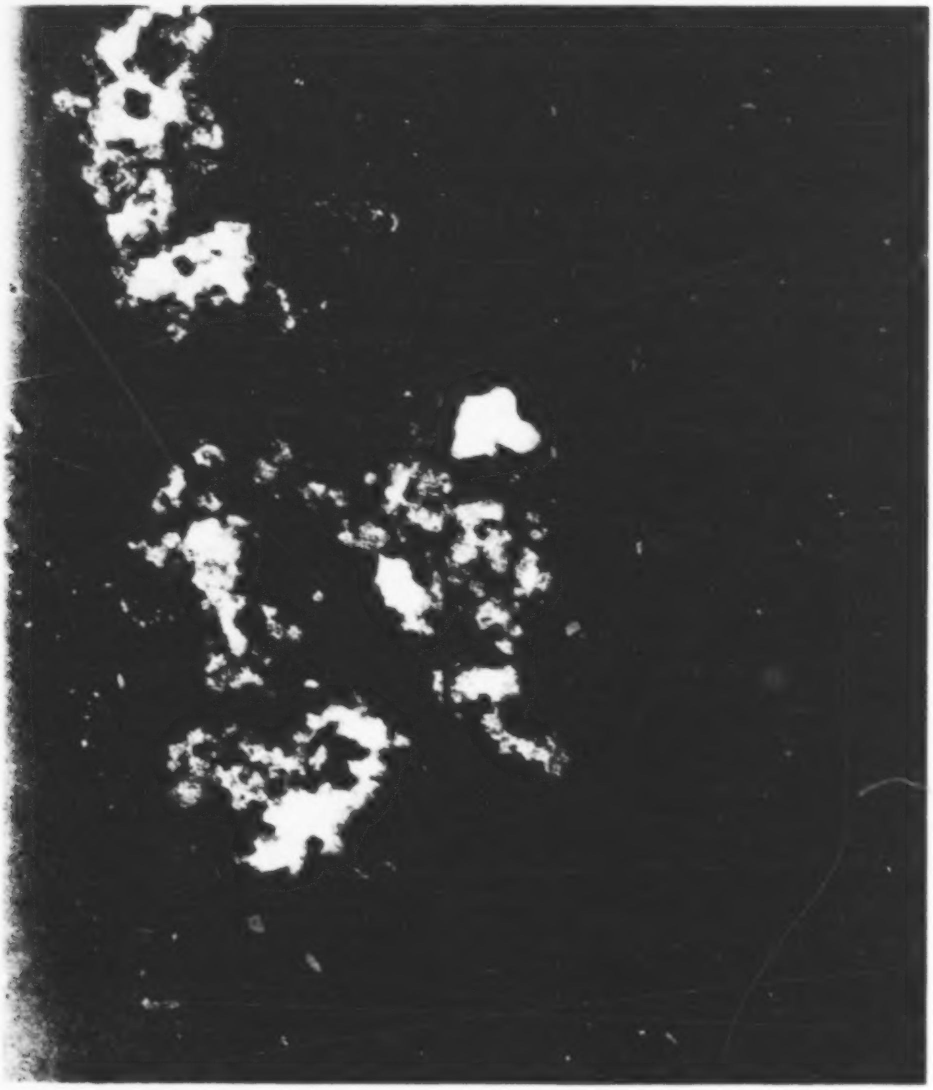

Figure 36. Cellular debris from secondary effluent as seen under the electron microscope. The black bar represents a distance of 1 micron or 0.000039 in. A freeze-drying method of sample preparation preserved the three-dimensional structure of the solid material which is shown in the dark shadows.

The most convenient measure of the colloidal content of water is its turbidity. Unfortunately, turbidity is not simply related to the weight of colloidal or suspended matter. Furthermore, larger particles, up to about 450 mμ, scatter proportionately more light per mg than smaller particles. The presence of a few floc fragments can produce erratic turbidity readings. Several light-scattering turbidimeters are available. Although it is not possible to calibrate different types of instruments to give comparable readings on a variety of suspensions, almost any light-scattering instrument can be used to show that the water is clear and free from turbidity. Well-clarified water will have turbidities of no more than a few tenths of a Jackson Turbidity Unit when the instrument is standardized with a dilution of a silica sol that has been measured by standard methods.

Viruses are colloidal components of wastewater that have significant public health aspects. Clarification by floc formation and filtration removes a large fraction of viruses. Although passage through a column of granular carbon is not expected to remove the remaining viruses, it does facilitate their inactivation by subsequent chlorine treatment. Water which had been batch-clarified, chlorinated and passed through a column of active carbon was found to have essentially zero chlorine demand. Free chlorine residuals (not chloramines) were maintained for days and viruses intentionally added were completely inactivated within one minute. The water met the USPHS Drinking Water Standards and was free from taste and odor. Chlorine probably does not physically destroy viruses but it does inactivate them so that they can no longer cause infection. Chloramines, formed when ammonia is present, are weak disinfecting agents.

DETERMINATION OF ORGANIC MATERIAL IN WASTEWATER

The amount of organic material in wastewater has traditionally been measured in terms of biochemical oxygen demand (BOD) or chemical oxygen demand (COD). Both have disadvantages which limit their usefulness in advanced waste-treatment research. The BOD requires 5 days between the time the sample is taken and the time when an answer can be obtained. It gives a measure of only biologically degradable organics and is not very accurate at the low concentrations found in the product water from several advanced treatment processes. The COD is a time-consuming analysis that is also subject to inaccuracies at low concentrations. A rapid and reasonably accurate measurement of the organic content to replace the traditional methods is required.

Carbonaceous Analyzer

One measurement of organic material that has proved to be convenient is the organic carbon content. Considerable work has been done using a dry oxidation system for determining total organic carbon (TOC). This system was developed by the Dow Chemical Company. The commercially available apparatus used for this determination is now referred to either as the Beckman Carbonaceous Analyzer* or, more frequently, as simply the Carbonaceous Analyzer. Several publications (4, 5, 6, 7) describing the application of this apparatus in the fields of waste treatment, wastewater renovation, and water pollution research have appeared recently. All the cumulative evidence to date shows that the Carbonaceous Analyzer is a valuable tool for any process or study involving measurable changes in organic carbon content.

A very slow and difficult task which is still far from complete has been to persuade individuals, long accustomed to thinking in terms of BOD and COD, to adopt the more-rapidly and accurately measured TOC as their main frame of reference. The work of Schaffer et al. (6) which was sponsored by the AWTR Program, helped significantly to further this. These authors described a thorough laboratory evaluation of the Carbonaceous Analyzer, followed by extensive field utility tests at a large municipal waste treatment plant. The laboratory studies included methods for removing interfering carbon dioxide and inorganic carbonates; ways of reducing particle size so that aqueous suspensions could be reliably analyzed; effects obtained by varying Analyzer sensitivity; sample concentration methods; determinations of TOC and COD for standard aqueous solutions of 32 different materials, about two-thirds of which were pure organic compounds, and one-third of which were natural products; and determinations of TOC and COD for raw sewage, primary and secondary effluents, and primary and secondary sludges.

These authors compared experimental and calculated TOC values for the 32 different standard materials mentioned above, with such TOC values being given for three organic-carbon concentration levels: 25, 5, and 1 mg/1. These authors also tabulated COD/TOC ratios for all 32 standards and for the previously mentioned sewage samples. From this laboratory evaluation, the authors concluded that the suitability, accuracy, and precision, both of the Carbonaceous Analyzer and of the analytical procedure used, had been "verified on a wide variety of organic compounds in water" down to a TOC concentration of 1 mg/l. They claimed that "one can expect an error of 0.15 to 0.20 mg/l in the mean of four determinations at the 0.6-mg/l carbon level." However, they added

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**Beckman Instruments, Inc., Fullerton, Calif.*

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later that "the practical lower limit of analysis is 1 mg/l carbon, with a precision of ± 0.2 mg/l" because of what they regarded as a small water blank.

Schaffer's field utility tests, conducted at a sewage treatment plant, permitted him to strike a reasonable, though not perfect, material balance for organic carbon. These tests also demonstrated the practicality of the sample preparation techniques and the utility of operation of the infrared carbon analyzer for the analysis of wastewater treatment process streams. Both COD and BOD correlated with TOC to the extent that the COD or BOD could be predicted within about ± 35 percent at the mean value from a determination of the organic carbon with a confidence level of 95 percent. Significantly better correlation probably cannot be expected because of the effects of toxicity, biodegradability, chemical structure, molecular weight, and susceptibility to chemical oxidants.

In a later study of river water samples with a wide range in organic content, a remarkably good correlation was found between COD and TOC. A linear plot had a correlation coefficient of 0.97. It should be pointed out, however, that more scatter in the data occurred in the low organic range that is of interest in advanced waste-treatment, than at high values. The relation between TOC and BOD was extremely poor.

From the TOC work that has been carried out, it has been found that the determination is more accurate than other methods as an indicator of organic pollution. This is due not only to the sensitivity of the measuring equipment, but also to the very high degree of carbon oxidation that takes place. The analysis is also more rapid than BOD and COD and is economical.

Carbon Analyzer Using Hydrogen-Flame Detector

Although carbon analyses with the Carbonaceous Analyzer are generally adequate for wastewater work, there are times when an instrument capable of accurate measurements at the 0.1 mg/l level would be desirable. Substantial progress toward filling this need has been made (8). The key component of this new apparatus is the hydrogen-flame ionization detector which has approximately 20 to 100 times the sensitivity of the infrared detector used in the Carbonaceous Analyzer. The exact sensitivity difference between these two detectors depends upon how the hydrogen-flame detector and its associated components are used. To carry out an alalysis with this new instrument, the aqueous sample is injected onto hot copper oxide in a combustion furnace where the carbonaceous material, even though in an atmosphere of helium, is oxidized

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to carbon dioxide. Hydrogen gas, in a heated catalytic reduction chamber packed with nickel-on-firebrick, reduces the carbon dioxide to methane at elevated temperature. The methane is swept into a hydrogen-flame detector, and the carbon content of the sample is determined from peak height using a strip-chart recorder. Inorganic carbonates must be removed before analysis by the same techniques that are required with the Carbonaceous Analyzer. As is the case for the Carbonaceous Analyzer, this new apparatus must be calibrated at least once per day if maximum accuracy is to be attained. However, since the new instrument is so extremely sensitive, very pure water is needed for preparation of the required standard calibration solutions; in fact, the purity of calibration water usually exerts more control over the attainable analytical limits of the method than does any other variable. Assuming optimum conditions for both the calibration and sample analysis steps, the limit of detection is about 50 micrograms/l of TOC; however, a more practical limit for which to strive is 100 micrograms/l (or 0.1 mg/l) of TOC. The time required for one analysis is approximately 60 seconds, and the reproducibility is ± 5%.

Ultraviolet Absorption Monitor

Another need that still exists in the field of organic analysis is instrumentation that can be used for continuous and automatic monitoring of advanced-process streams. There is carbon analysis equipment available, but it has certain disadvantages. An approach that seems to have potential is measurement of ultraviolet absorption. This approach is based upon the fact that many of the organic pollutants found in water strongly absorb in the ultraviolet region. At the same time, those types of organics which are UV absorbers tend to be the relatively toxic organic compounds. These include simple aromatics, polynuclear hydrocarbons some of which are carcinogens, and chlorinated hydrocarbon pesticides. Whereas neither BOD, COD, nor TOC determinations can furnish any indication of the kinds of organic compounds present, UV absorbance monitoring is capable of showing the presence of possibly dangerous organic types or classes.

Extensive intramural work has indicated that UV absorbance monitoring will probably be useful, or perhaps even necessary, at certain points in an advanced treatment system. Preliminary spectrophotometric scanning of a membrane-filtered secondary effluent, both before and after treatment with activated carbon, showed the occurrence of only a slightly sloping plateau between 250 mμ and 260 mμ. This meant that the required instrumentation might be able to employ the strong, and very sharp, monochromatic radiation at 253.7 mμ produced by a low-priced, cold-cathode mercury lamp fitted with a simple interference filter. The usual expensive monochromator would not be required. Additional studies of clarified and carbon-column-treated secondary effluents from different sewage sources confirmed this and also indicated that an acceptably linear correlation existed between TOC and UV absorbance, both for the column feeds and for the final column effluents. This, in turn, meant that UV absorbance measurements might yield indirect, but satisfactory, measurements of TOC.

On the basis of these preliminary data, plus certain theoretical considerations, a lengthy study involving UV-TOC monitoring of the carbon-column adsorption process was conducted for 258 days at the Lebanon Pilot Plant. This was a column "profile" study wherein daily grab-samples were collected from the column feed, final column effluent, and several intermediate points along the column. Each of the daily samples was then measured for a wide variety of information, part of which included TOC (carbonaceous Analyzer) and UV absorbance (Beckman DU).

In addition to UV data for daily grab-samples, continuous UV measurements were made at just one sampling point at any given time by means of an industrial UV Monitor. This apparatus was a duPont Model 400 Photometric Analyzer*.

One important discovery, during this pilot plant study, was that the presence of significant amounts of chloramines, particularly monochloramine, may interfere with UV monitoring unless countermeasures are taken. Ammonia in a typical secondary effluent does not interfere at 253.7 mμ, even when present in concentrations up to 25 mg/l as nitrogen. If, however, chlorine is added to inhibit biological decomposition of organic matter, as was the case for the clarified column feed, then this ammonia is converted into interfering chloramines. Chloramines tend to be removed by a carbon column, usually within the first one or two feet of carbon depth, expecially if the carbon is relatively new. Therefore, UV monitoring past a bed-depth of one foot typically was free from chloramine interference. However, most UV data for the chlorinated column feed and for grab samples taken at the one-foot bed-depth required corrections. These corrections were made using an experimentally determined relationship between absorbance error and ammonia content.

A simple linear regression was performed on the UV-TOC data for the column feed and, individually, for the one, two, three, and four-foot depths of carbon. The resulting linear correlation coefficients were 0.85 for the column feed and from 0.89 to 0.93 for the four carbon depths. When the UV-TOC data for these four carbon depths were then pooled and recomputed, the linear correlation coefficient for the combined data was 0.93. Thus, the evidence is strong that a single linear function adequately represents the relationship of UV absorbance to TOC at four different depths of carbon.

**Equipment loaned by Instrument Products Division, E. I. duPont deNemours and Co., Wilmington, Del.*

In spite of such good correlations, there are reasons why further studies should be made before we can conclude that UV absorbance measurements are a generally satisfactory substitute for determinations of TOC. The results described were obtained at only one sewage treatment plant and by the application of only one clarification procedure, one method of column feed preservation, and one type of carbon-column treatment. Unless eliminated in some convenient way, perhaps automatic, chloramine interferences will always place severe restrictions on the manner in which UV monitoring can be used and perhaps on the reliability of the UV data. Only the avoidance of chlorination will prevent this constant possibility of chloramine interference. The presence of certain kinds of turbidity or of many dissolved heavy metals (e.g., iron) leads to erroneously high UV values. Neither of these two factors probably caused UV interference during the 258-day Lebanon column study because the lime clarification step would tend to remove both heavy metals and turbidity. However, recent studies of the UV-TOC relationship for a municipal tap water, river water, and several primary and secondary sewage effluents have in no case yielded acceptable linear correlations even after reduction of any chloramines present. Thus, a considerable amount of research remains to be done.

It is quite possible that the most useful application for UV absorbance measurements will consist of continuous monitoring of the final product from an advanced treatment system. Although the correlation between organic matter and UV absorbance is not perfect, any foreseeable breakdown of the process that would liberate organic matter or turbidity would also produce high UV absorption. Most of the objectionable refractory substances which can be removed on carbon are also good absorbers of UV light. Even though UV absorption is not sensitive enough to detect the lower toxic levels of some pesticides or carcinogens, these compounds would in practice be associated with much larger quantities of other UV-absorbing substances. Since most organic UV-absorbing substances are expected to be absorbed on carbon, a UV detector will provide a useful indicator of the efficiency of a carbon process.

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